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Corrosion degradation and prevention by surface modification of biometallic materials

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Abstract Metals, in addition to ceramics and polymers, are important class of materials considered for replacement of non-functional parts in the body. Stainless steel 316, titanium and titanium alloys, Co–Cr, and nitinol shape memory alloys are the most frequently used metallic materials. These alloys are prone to corrosion in various extents. This review briefly discusses the important biomaterials, their properties, and the physiological environment to which these materials are exposed. Corrosion performance of currently used metallic materials has been assessed and threat to the biocompatibility from corrosion products/metal ions is discussed. The possible preventive measures to improve corrosion resistance by surface modification and to increase the bioactivity of the metallic surfaces have also been discussed. Importance of the formation of oxide layers on the metal surface, another aspect of corrosion process, has been correlated with the host response. The gap areas and future direction of research are also outlined in the paper.

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1 Introduction to bioimplant materials: general issues and concerns

Man-made materials and devices have been developed to replace diseased or damaged parts (which become non-functional) in the human body in order to prolong life, to improve and restore tissue function, and to improve quality of life. Significant developments have been taking place to provide suitable biomaterials from metals/alloys, ceramics, bioglasses, and polymers with minimal reaction and rejection by the body. [1–3]. Table 1 showed the types, applications, and major failure mechanism of various biomaterials including metallic/alloys. However, each of these has some limitations. A single material cannot offer all desired properties; therefore, they have been used in combination with each other in the form of coatings and joints. Table 2 lists metallic alloys used in biomedical applications with their major alloying constituents and relative usefulness. These metallic materials form a major portion of biomaterials mainly due to their strength and good fabrication properties; however, their biological response and tendency to corrode are of serious concern in using them as orthopaedic components [1, 4–6].

This paper briefly reviews the corrosion of various metallic biomaterials vis-à-vis chemistry of physiological environments and corrosion mitigation using different surface modification techniques. The directions for the future work have also been outline at the end.

1.1 Biological response to metallic implants

Biocompatibility is the primary requirement for biomaterials. Biocompatibility of implant devices relies on

Table 1 Types of biomedical materials and their applications

Biomaterials	Objectives	Degradation mechanism	Applications
Metals/alloys SS316L, Co–Cr alloys, Ti and Ti alloys, Ni–Ti alloys	Load bearing	Corrosion and mechanical	Fracture fixation plates, screws, pins, nails, joint replacements, orthodontic wires, femoral stems, cases for pacemakers, supports for heart valves, dental implants, dental crowns, bridges, fillings, and inner ear bone replacements
Ceramics Carbon coatings, alumina, oxides, zirconia, glass, glass ceramics, and hydroxy apatite (HAP)	High hardness, wear resistance, and better bone bonding	Corrosion and mechanical	Carbon in heart valves, dental implants, joint implants, coatings for dental and joint implants, fill bone voids/cavities by HAP, tissue scaffolds, drug delivery systems, and inner ear implants
Polymer Ultra high molecular weight polyethylene, polyester, polytetraflouroethylene, PMMA, hydrogels, silicone rubber, PGA/PLA, collagen, cellulose, and chitosa	Articulating surfaces	Wear, swelling, leaching, chemical	Joint replacement, vascular grafts, bone cement, orthodontic devices (e.g. plates, dentures) contact and intraocular lenses, catheters, hand and toe joints, artificial tendon and ligament, reconstructive surgery, sutures, staples, tissue scaffolds, drug delivery systems, and hemostatic bandages, pace maker leads.

Table 2 Characteristics of strategic orthopaedic metallic materials [3]

Characteristics	Stainless steels	Cobalt-base alloys	Ti and Ti-base alloys
Designation	ASTM F-138 (316 LDVMO)	ASTM F-75 ASTM F-799 ASTM F-1537 (cast and wrought)	ASTM F-67 (ISO 5832/II) ASTM F-136 (ISO 5832/II) ASTM F-1295 (cast and wrought)
Principal alloying elements (wt %)	Fe (balance) Cr (17–20) Ni (10–14) Mo (2–4)	Co (balance) Cr (19–30) Mo (0–10) Ni (0–37)	Ti (balance) Al (6) V (4) Nb (7)
Advantages	cost, availability, processing	wear resistance, corrosion resistance, fatigue strength	Biocompatibility corrosion resistance minimum modulus fatigue strength
Disadvantages	long-term behavior, high modulus	high modulus	low wear resistance, low shear resistance
Application	temporary devices (fracture plates, screws, hip nails) used for THRs stems	dentistry casting, prostheses stems load-bearing components in TJR (wrought alloys)	in THRs (with modular Co-Cr-Mo or ceramic) femoral heads, long-term permanent devices (nails, pacemakers)

several issues, as illustrated in Fig. 1, which ultimately affects the performance of implant device. Inappropriate design of the implant devices, unwanted device degradation/corrosion and/or development of adverse host tissue reaction can lead to device failure. A foreign material when placed in or entered the human body as a result of corrosion process, tissue reacts with it in a variety of ways (Fig. 1). These reactions are usually highly undesirable and have the potential to lead to reactions such as chronic inflammation and or hypersensitivity. Hypersensitivity, is either immediate or delayed response due to the contact with metals, corrosion products or metallic salts and is fairly common, affecting more than 15% of the population [7, 8]. Metal ions may also be associated with problems such as cytotoxicity, genotoxicity, carcinogenicity, etc.

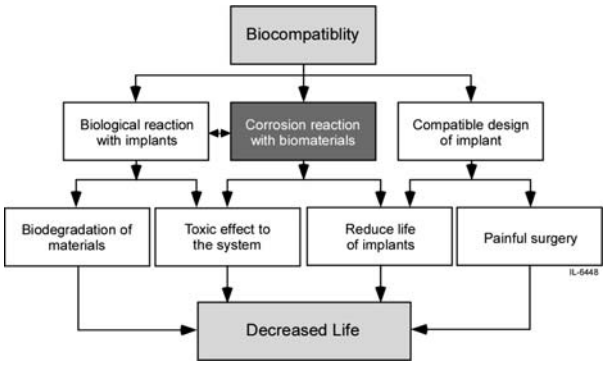


Fig. 1 Factors and their effects on biocompatibility

There are numerous metallic elements, which act as sensitizers to above mentioned problems and, are therefore, undesirable or intolerable beyond certain limits. Most metal ions have ability to form complexes with native proteins, such metallo-organic complexes can induce allergy or may act as allergens in the body. Some of these metals are beryllium [9], tantalum [10], titanium [11, 12], and vanadium [10, 13], the most common metal sensitizers being nickel [1] followed by cobalt [9] and chromium [12]. Such sensitizers are present in commonly used biomedical alloys in significant quantities. For example, in stainless steel, Ni: 13–15%, Cr: 17–19%, and Mo: 2–4%; in Co–Cr alloy, Ni ~1%, Co: 62–67%, Cr: 27–30%, and Mo: 5–7 %; and in Ti alloys: Ti: 89–91%, Al: 5.5–6.5%, and V: 3.5–4.5% (all values are in wt%). Nickel is a well known for its toxicity and propensity to cause allergies. Figure 2 [14]

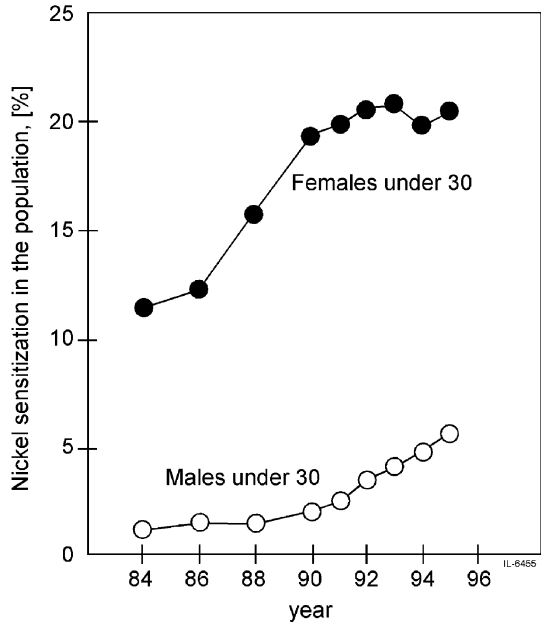


Fig. 2 Human population affected by nickel sensitivity [14]

shows how the human population is affected by nickel sensitization. In one of the earliest case studies implicating an orthopaedic implant as a source of metal sensitivity, a twenty-year old woman was seen with extensive eczematous dermatitis on the chest five months after stainless-steel screws were implanted to treat a chronic patellar dislocation [15]. Treatment with topical corticosteroids abrogated the condition for one year, after which it worsened, with increased generalized dermatitis, and resulting in the removal of the stainless steel screws. The day after screws were removed, the eczema subsided, completely disappearing within 72 h. Another similar report appeared on cobalt hypersensitivity from cobalt-alloy plates and screws used to fix a fracture of the left radius and ulna in a forty-five-year-old woman [16]. The patient developed periprosthetic fibrosis, patchy muscular necrosis, and chronic inflammatory changes peripherally seven years after implantation. After removal of all metal implants, the swelling disappeared, and eventually the patient became symptom-free, however, there remained a hypersensitivity to cobalt, as demonstrated by patch testing.

Cytotoxicity is a toxic effect due to various elements at cellular level that causes the death/alteration of the cellular membrane or that inhibits enzymatic metabolic processes. The genetic toxicity (genotoxicity) may cause mutagenic effects that damage or change the genes or chromosomes. Finally, the carcinogenic elements can help developing neoplastic lesions (tumors) in the body, though their inductions are rare. Carcinogenic potential of metal ions largely depends on their oxidation state, solubility, concentration, etc. However, the underlying molecular mechanism of carcinogenicity of metal ions is yet not well understood. This, knowledge of effects and the mechanisms of reaction of a particular foreign element with the tissues is essential when selecting the material for manufacturing medical devices.

1.2 Corrosion of metallic material in physiological environment

Corrosion is an inevitable, deteriorating reaction when metallic materials come in contact with an environment such as liquid, gaseous or combination thereof. The physiological solution (body fluid) is considered extremely corrosive to metallic materials. The corrosion of metallic implants due to the body environment can effect the human life in different ways: (i) it may release undesirable metal ions/corrosion products which are non-biocompatible, ii) it may reduce the life of implant device and therefore, may impose another

costly and painful surgery, and iii) ultimately reduce the human life (Fig. 1). For instance, the corrosion of a stainless steel implant releases iron, chromium, and nickel ions; titanium and titanium alloy implants release titanium, vanadium, and aluminum ions; and Co–Cr implants are known to release chromium and cobalt ions [1–13]. The release of metal ions depends also on the success of the implant procedure and functioning. For example, patients with well-functioning Ti-alloy total joint replacement components had as much as a threefold increase in the concentration of Ti in their serum. In patients with a failed total joint Ti alloy components, there was as much as a 50-fold increase in serum Ti levels compared with controls without implants [17]. Dissolved metal ions can accumulate in tissues as well as near the implant or may be transported to other parts of the body. For example, after 10–13 years of residence of 20 stainless steel Charnley hip arthroplasties in the human body, a significantly higher concentration of metallic species in body fluid was observed as compared to that without implant. This included Ni concentration in blood of ~0.51 μg/L, in plasma of ~0.26 μg/L and in urine of ~2.24 μg/L, and Cr level in plasma of ~0.19 μg/L. Similarly, the Ti concentration of ~135.57 μg/L was found in the serum of patients with failed Ti–6Al–4V total knee replacements after 57 months which was much more than in the control [18]. In one of the in-vitro studies, the experiment was designed to simulate the worst case of prosthesis loosening, the debris generated between bone and titanium alloy was found at the rate of 0.3–1.1 μg per load cycle and was considered to be the higher limit [19]. Others found approximately 1 μg/L concentration of titanium in blood serum of patients with stable titanium prosthesis; however, that, reportedly, could increase upto 4 μg/L in case of mobilized prostheses [20].

Metallic biomaterials corrode in variety of ways including general and localized corrosion types. Extensive research [21–114] has been carried out on to understand the dominant forms of corrosion that biomaterials commonly experience and their implications to biological and mechanical functions of the human body. However, electrochemical enhanced wear [21–27], fretting [28], fatigue [29–36], pitting/crevice [45–48] and galvanic corrosion [49–61] are the most commonly observed.

1.3 Role of components of physiological environment in corrosion of metallic materials

The functionality of biomaterial devices in the body greatly depends on the chemistry of the biofluid surrounding the implant. Biofluids (physiological solution), inside tissue cells (intracellular fluid) or outside tissue cells (extracellular fluid) carry several organic and inorganic materials to the need of body. Extracellular fluids are of two types, blood and interstitial fluid. Other extracellular body fluids that occur in smaller amounts are urine, digestive juices, and cerebrospinal fluid. Chemically, blood (plasma) and interstitial fluid (including lymph) are similar while intracellular fluid is chemically different from the extracellular fluids. Body fluids are reported to be a complex and composed of salts, trace metals, amino acids, sugars, proteins, cells, etc. [115]. These components of the body fluid produce anions such as chloride (Cl^-), phosphate (PO_4^-), and bicarbonate (HCO_3^-) and cations such as potassium (K^+), sodium (Na^+), calcium (Ca^+), and magnesium (Mg^+). Body fluid is a buffer solution. The pH of the normal blood and interstitial fluid usually remains between 7.35–7.45, however, it may decrease to 5.2 during implantation in hard tissues, and should return to its normal pH within two weeks of time while the temperature remains about 37°C [116]. The high Cl^- concentration among various anions is considered to accelerate corrosion of implants that can lead metal ion release and disturbances in trace metal ions. The latter can change the biochemical reactions and associated physiological pathologies. For instances, change in Fe contents can either lead to anemia (when it is in low dosage) or may damage the liver by high Fe dosages. In order to develop artificial body fluids, usually, those mineral components of the natural products are included that have shown effects on the processes [117]. However, most of the in-vitro corrosion studies have been conducted in synthesized solutions by adding different chloride containing salts that show significant effects on corrosion processes. A few studies have also been conducted in solutions containing organics, such as protein substances, primarily to investigate their effect on corrosion processes in implant materials [118–123]. These studies emphasize that even small changes in corrosion can, over the lifetime of device, result in big difference in metal ion release, and therefore, it is important to further understand how/why devices do function for the lifetime of the patient.

Corrosion studies on orthopaedic biomaterials have been frequently carried out in Hank's solution, Ringer's solution, and artificial saliva. Hank's solution is a salt solution that is made from $CaCl_2$, $MgSO_4{\cdot}7H_2O$, KCl, KH_2PO_4, $NaHCO_3$, NaCl, $Na_2HPO_4{\cdot}2H_2O$, and d-glucose while Ringer's solution contains NaCl, $CaCl_2$, KCl, and $NaHCO_3$ in de-ionized water. Materials for dental application have been studied by investigating

their corrosion resistance in synthetic saliva. Various formulations have been suggested which are supposedly close to the natural saliva. A review that included about 60 different artificial saliva formulations, including SAGF (Saliva Gal-Fovet), described the role of various chemical species in the formulae [117]. The review also focused upon the role of buffering, CO_2 gas, calcium ions, hydrogenocarbonates, hydrogenophosphates, and thiocynates on biological and physicochemical processes in the body. Main constituents of artificial saliva are Ca^+, CO_3, $P_{inorg\ tot}$, Mg^+, Na^+, SCN^-, Cl^-, NH_4^+, and the pH is near neutral. In addition to these ions, fractions of organic compounds, such as glucoproteins, have been reported in the saliva and have an important role in maintaining the viscosity which, in turn, affects the diffusion of various ions [123, 124]. Their affect on the corrosion of bio-materials is not well established. Some of the reported compositions of saliva are briefed in Table 3 [117–129].

1.4 Standard tests for evaluation of corrosion in physiological environment

Following are some of the standard methods specifically employed, other than commonly used such as ASTM G 61–86, ASTM G 5-94, as guidelines for evaluating the corrosion performance of metallic biomaterials

1.4.1 ASTM G71-81

This is a standard guide for conducting and evaluating galvanic corrosion tests in electrolytes. This provides laboratory and field-testing procedures for estimating the galvanic corrosion between two dissimilar metals/alloys in an electrolyte that does not cause erosion-corrosion or cavitations. Galvanic current and potential of the couple are recorded and are used to represent performance of the galvanic couple. These may be compared with the individual components of the couple to show their relative performance.

1.4.2 ASTM F746-87

This is a standard test method for pitting or crevice corrosion of metallic surgical implant materials. This test is designed for the evaluation of pitting and crevice corrosion of bio-implant materials such as stainless steel. A series of potentials above and below the pitting potential of a sample is applied to activate pitting and to allow the repassivation of the pits. The corrosion current is continuously monitored during the test as the potential changes. The potential at which pits no longer passivate is considered to be a critical pitting potential.

1.4.3 ASTM F2129-01

This is a standard test method for conducting cyclic potentiodynamic polarization measurements to determine the corrosion susceptibility of small implant devices. This test method is used to assess the corrosion susceptibility of small, metallic implant devices or components using cyclic (forward and reverse) potentiodynamic polarization. Examples of device types, which may be evaluated by this test method, include vascular stents, filters, support segments of endovascular grafts, cardiac occluders, aneurysm or ligation clips, and staples. This test is used to assess a device in its final and finished form when it is ready to implant, and small devices should be tested in their entirety. Because of the variety of configurations and sizes of implants, this test method provides a variety of specimen holder configurations.

The electrochemical parameter for any specific material may greatly depend on the methods used for its determination [130]. For instance, pitting potential obtained by using ASTM G61 may not be the same as by ASTM F746. Hence the recommendation from the two techniques may be entirely different [131, 132]. Table 4 illustrates the pitting potential of some biomaterials obtained by using different methods.

Table 3 Composition (M mol/L) of some of the artificial saliva

Ca^{++}	CO_3	Mg^{++}	K^+	Na^+	$C1^-$	SCN^-	P	NH_4^+	pH	Ref.
5.80	000	00e	58.60	14.64	32.19	00	16.79	00	6.7	117
00	7.10	00	00	27.14	29.80	2.5	4.70	4.10	6.8	124
00	00	00	25.74	28.16	29.84	2.24	4.7	4.1	–	125
00	17.85	00	21.48	33.49	28.07	3.4	2.98	00	6.7	126
1.43	6.45	00	20.5	11.55	23.22	2.3	5.1	4.35	–	127
1.5	15.00	00	00	37.5	3.00	00	15.00	00	–	128
1.0	17.86	00	00	51.14	37.08	00	1.0	00	–	129

Table 4 Pitting potentials of some biomaterials determined by various methods

Material	Electrolyte	Pitting Potential, mV	Experimental Technique	Reference
316L	Deaerated, pH-7.4, Hank's solution, 37°C	+280	Potentiodynamic	43
316L	0.9% NaCl solution, 40°C	+400	Do	132
316L	Do	+130	ASTM F746	132
HA coated 316L	Deaerated, pH-7.4, Hank's solution,	+449 to +567	ASTM G61	289
316L	Deaerated Hank's solution	+352	Do	289
316L	Deaerated, pH-7.4, Hank's solution, 37°C	+280	Do	44
316L	Artificial saliva at 40 °C	+400	ASTM G61	132
316	Hank's solution, at 37°C	+350 to +400	ASTM G61	229
Ti–6Al–4V	Hanks solution at 37°C	> +1000	Do	229
Ti–6Al–4V	Deaerated Hank's solution, 37°C	+1900	Do	44
Co–Cr	Deaerated Hank's solution, 37°C	+650	Do	44
Ni–Ti	0.9% NaCl at 40°C	+100 to +200	ASTM F746	132
Ni–Ti	0.9%NaCl at 40°C	+400	ASTM G61	132
Ni–Ti	Artificial saliva at 40°C	~ +1000	ASTM G61	132
Ni–Ti	Hank's solution at 37°C	~ +650	ASTM G61	132

2 Strategic biomaterials and their degradation

2.1 Stainless steels

Stainless steel 316L has been widely used in biomedical applications as a prosthetic material due to its lower cost, excellent fabrication properties, good corrosion resistance, and easy availability [2, 131–142]. The composition of stainless steel is standardized in ASTM F138 and F139 (C ≤ 0.030, Mn ≤ 2.0, P ≤ 0.025, S ≤ 0.010, Si ≤ 1.0, Cr-7.0–19.0, Ni-13.0–15.0, Mo-2.25–3.5, N ≤ 0.10, Cu ≤ 0.50, Fe-Balance, all in wt%) to have a single austenitic phase (without delta phase). Alloying elements such as chromium (Cr) provides oxidation resistance while molybdenum (Mo) and nitrogen enhance the localized corrosion resistance of austenitic stainless steel [136–142]. Other varieties of stainless steels, REX734 (C < 0.06, Cr-21.00, Ni-9.37, Mn-4.00, Mo-2.20, N-0.40 all in wt%) and nickel free P558 (C-0.20, Cr-17.35, Ni-.08, Mn-10.18, Mo-3.09, all in wt%) are also being developed and introduced for biomedical applications [134, 135]. REX 734 has been shown to be suitable for joining in certain types of implants such as monobloc hip stems and spine systems, and even in the annealed condition they have high strength, high work hardening rate (large strength potential for work-hardening in semi-finished products), and high corrosion resistance at competitive price. However, P558 is being developed to reduce the risk of nickel; and its mechanical and corrosion properties were found to be superior to SS316L and REX 734 in Hank's body solution. Other than by changing composition, performance of existing stainless steel for biomedical purposes, can be enhanced by introducing cold deformation [143–146].

As mentioned earlier, the host bio environment contains a high concentration of chloride ions, which reduces the pitting resistance of stainless steel. The limited pitting potential of stainless steels in physiological solutions has been reported by several researchers [147–150]. The stainless steel implants are often degraded due to pitting, crevice, corrosion fatigue, fretting corrosion, stress corrosion cracking, and galvanic corrosion. These corrosion mechanisms may produce defects in the implants to make them non-functional and may also enhance the metal ion concentration in surrounding tissues. A survey of eleven surgically retrieved stainless steel implants showed that they were failed due to the aseptic cup loosening and stem cement debonding. [147]. Obstruction or removal of passive film such as due to variation in electrochemical may reduce the fatigue strength of stainless steel implants as shown by the Fig. 3 [36, 64].

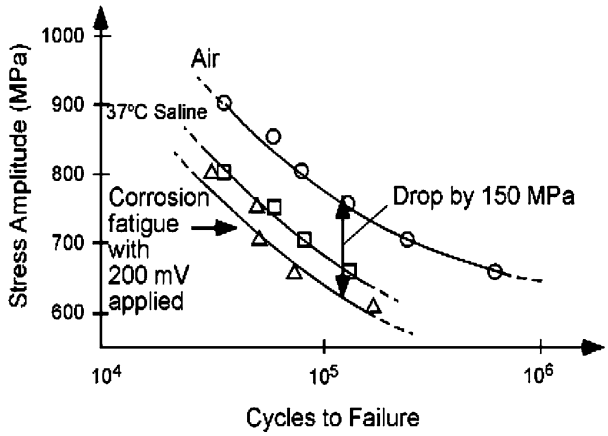


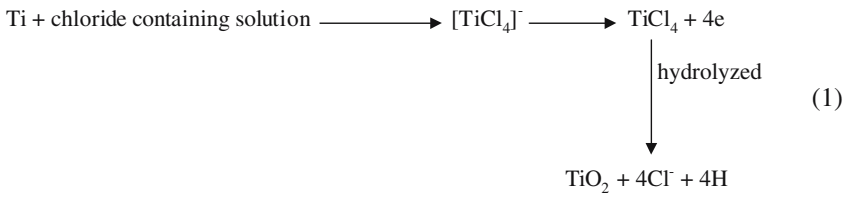
Fig. 3 Effect of potential on corrosion fatigue of stainless steel 316 [36, 64]

Corrosion of stainless steel, especially SS316L in the bio-environment has been a subject of extensive research with a special emphasis on the release of metallic ions into the tissues surrounding the implants [42, 148–157]. Metal ion release and its deleterious effects on tissue functions have been studied by conducting both in-vitro as well as in-vivo experiments. In one study [152], rat bone marrow was exposed to a stainless steel slurry with the aim of observing the effect of corrosion products on bone marrow. It has been inferred that corrosion products, beyond certain concentrations, obstruct the normal behavior of the rat bone marrow culture. The metal ions from corrosion reaction have been shown to interfere with the proliferation and differentiation of osteoblastic cells. These ions may also cause sensitization [153] and the risk of tumors [154, 155]. Also, the particulate debris may lead to osteolytic and mechanical failure of the implants [156–158]. Orthodontic appliances made from SS304 and SS316 release Ni, Cr, and Cu, though the quantities are low enough not to cause serious health hazards [158]. The concentration, however, was higher at acidic versus alkaline pH [158]. The corrosion product from stainless steel 316L implanted in the femur (as a part of an artificial hip) was found to consist of chromium, sulfur, iron, phosphorous, calcium, and chlorine [159]. The oxide layer formed on the surface of implanted SS316L (in the human body) was found to contain calcium and phosphorous in addition to other metal ions [160]. The release of metal ions from SS316L was forced by corrosion at various electrochemical potentials in a modified Eagle's culture medium. The different concentrations of metal ions (corrosion products) affected the toxicity and cell growth [161]. Results indicated that the toxicity of the corrosion product was more prevalent when the nickel concentration exceeded 11.7 ppm. This made the smooth growth of vascular muscle cells difficult. Metallic ions and corrosion products have also been noticed to change the cell morphology and to induce cell necrosis [162].

In order to reduce the release of metal ions from and to increase the corrosion resistance of stainless steels, several biocompatible coatings such as thermally grown oxides, electrolytically grown oxides and hydroxyapatite (HAP), have been investigated [131, 159, 162, 163]. The oxide films were grown on SS316L by different methods including but not limited to thermal exposure (poly-crystalline and amorphous oxide), proprietary processes, and electropolishing (in a phosphoric acid-glycerine solution). The corrosion characterization of thermally grown amorphous oxide surface layer on 316L in Ringer's solution showed that the oxide was more resistant than the bare 316L and other oxides [162, 163]. In a corrosion study carried out on hydroxyapatite (HA) coated SS316L in Ringer's solution [131, 159], a positive shift in the OCP (open circuit potential) was an indication of a stable coating/insulation behavior [131]. On the other hand, the OCP of bare SS316L showed a negative shift and enhanced metal dissolution. The pitting corrosion resistance of other HA coated stainless steels also improved compared to uncoated SS316L. The two layer coating composed of HA/Ti on SS316L was reported to be more corrosion resistant than the single HA layer on SS316L when tested in a 0.9 wt% NaCl solution at 37°C [159]. It also demonstrated good osteointegration suggesting its usefulness as an endodontic implant. Coatings on stainless steels however, have certain limitations due to the susceptibility of stainless steels to crevice corrosion that results in breaking or flaking off of the coating and may cause severe material degradation.

2.2 Titanium and Titanium alloys

During last more than 50 years, titanium has been commercially available and several titanium alloys have been developed. It was not used much as a surgical alloy until 1960. However, since mid 1970, its use has been increasing steadily [164–167]. Among various titanium alloys, including commercially pure (CP) titanium, Ti–6Al–4V accounts for about 50% of the total market for biomedical applications and has become a standard biomedical alloy. Titanium (melting point 1678°C) undergoes an allotropic transformation from the hcp structure (α-phase) to a bcc structure (β-phase) above the temperature of 882°C (beta-transus) [168]. This transformation results in the existence of different structural forms, namely α, β, and $\alpha + \beta$ or metastable β. Alloying elements are added to stabilize both of the phases. Aluminum is added as an α-stabilizer while vanadium, molybdenum, and iron are added as β-stabilizers. Titanium and its alloys have excellent corrosion resistance and mechanical properties. Titanium alloys have very high pitting potentials, which is the reason for their being increasingly used for biomedical applications [44, 76, 169, 170]. High corrosion resistance of titanium and titanium alloys is due to the thermodynamically stable TiO_2, though there are various other oxides on titanium alloys that are also reported to form on the surface, as listed in Table 5 [38, 171]. A few nanometer thickness of TiO_2 is often formed in most of the biological environments according to the following reaction: [167, 172–175].



(1)

Table 5 Types of oxide form on titanium and titanium alloys [38, 171]

Material	TiO_2	Al_2O_3	Nb_2O_5	MoO_3/MoO_2	ZrO_2
CP Ti	Yes	Yes	No	No	No
Ti–6Al–4V	Yes	Yes	No	No	No
Ti–5Al–2.5Fe	Yes	Yes	No	No	No
Ti–6Al–7Nb	Yes	Yes	Yes	No	No
Ti–15Mo–5Zr–3Al	Yes	No	No	Yes	Yes

Titanium oxide exists in various stoichiometric and crystallographic forms. Some of the known forms of titanium oxide and their physical properties are presented in Table 6 [176].

The high affinity of titanium to oxygen is advantageous in regenerating a protective passive film. Despite showing stable film characteristics and resistance to corrosion, results from in-vivo tests showed marked differences in the thickness and composition of the passive film for various titanium implants. The film was found to change with the implantation time and became thicker with time [174–179]. The film also incorporated other mineral ions, such as calcium and phosphate into it from the physiological solution [174, 175]. The oxide layer formed on titanium (after implantation in the human jaws) was also found to contain calcium, phosphorous, and sulfur [177, 178]. When titanium was immersed in Hank's solution containing albumin, a heterogeneous and porous apatite containing albumin film was reported to form [179]. The preferential absorption of phosphate ions on the titanium oxide film was noticed as first stage of the precipitation [179]. An other favorable aspect of titanium oxide is its ability to help bone in-growth. This has, therefore, encouraged many researchers and scientists to modify the surface of titanium and its alloys with suitable oxides to enhance their corrosion resistance and bioactivity [180–182]. However, the corrosion response of such modified surfaces has not been thoroughly studied.

Self-healing and the healing rate of passive oxides are important issues when materials are under wear-corrosion or fretting-corrosion situations (in such situations, the oxide film is repeatedly damaged by the mechanical forces). The regeneration of a passive surface layer on the titanium surface in in-vivo environment is slow. The regeneration rate of the film has been slower in Hank's solution (closer to body fluids) than in saline water [183]. This, in turn, increases the release of titanium ions and was evident in the tissues adjacent to the titanium implants [184–187]. In spite of the stable passive film, the increase in in-vivo corrosion of titanium, was speculated to be due to the hydrogen peroxide (H_2O_2) generated by the biological system which plays an important role in the corrosion reaction [183–188]. A few studies conducted on titanium corrosion in H_2O_2 containing phosphate buffered saline solutions showed an increase in the corrosion rate of titanium with increasing peroxide dosages [185–190]. The repassivation of various titanium alloys (Ti–6Al–

Table 6 Properties of titanium oxides

Name	Formula	Ti–O Bond length (Å)	Density (g/cm^3)	Color
Anatase	TiO_2	1.91	3.90	White
Brookite	TiO_2	1.84–2.03	4.13	
Rutile	TiO_2	1.988	4.27	
Ti Sesquioxide	Ti_2O_3	–	4.486	Purple–Violet
Ti Oxide	TiO		4.888	Gold/Bronze

4V, Ti–6Al–7Nb, and Ti–13Nb–13Zr), in phosphate buffered solutions (PBS), bovine albumin in PBS, and 10% foetal calf serum in PBS at different pH levels was evaluated by a change in hardness. It was found that corrosion reduced the hardness of surface oxides in all of the alloys. The maximum reduction in the hardness was observed in the presence of bovine albumin. It was concluded that the protein in the environment interacted with the repassivation process and changed the hardness of the surface oxide [191].

Although the Ti and Ti–6Al–4V alloys exhibit excellent resistance against general and pitting corrosion, the low wear resistance and the possibility of vanadium release from Ti–6Al–4V may induce aseptic loosening during long-term implantation [191, 192]. Further, the susceptibility of Ti–6Al–4V to hydrogen assisted stress corrosion cracking and fretting fracture in the saline solution, shown by Fig. 4 [79] and Fig. 5 [36, 85] respectively, question the long term reliability of titanium based devices. This has led to the development of new alloys without vanadium, useful for biomedical devices. These alloys include Ti–15Mo–3Nb, Ti–Mo–Nb–Al, Ti–Mo–Nb–Al–Cr–Zr, Ti–13Zr–13Nb, Ti–15Zr–4Nb, Ti–6Al–7Nb, Ti–Zr–Nb–Ta–Pd, Ti–Mo–Nb–Al, Ti–Mo–Nb–Al–Cr–Zr, Ti–Zr–Nb, and Ti–Zr–Nb–Ta–Pd [193–196]. To obtain low rigidity alongside other properties, the development of single phase β-titanium alloys has also proven to be remarkably good for biomedical applications. A Young's modulus close to that of bone is desirable for biomaterials because materials with high moduli can cause bone resorption [14]. The Young's moduli of currently used biomaterials, in decreasing order, are indicated below

$$\text{Co} - \text{Cr} - \text{Mo} < \text{SS316L} < \text{Ti} - 6\text{Al} - 4\text{V}\ (\alpha + \beta \text{ type}) < \beta\text{-Ti alloys} \tag{2}$$

The Young moduli of β-Ti alloys are close to that of cortical bone (<30 GPa). The other benefits of β-Ti alloys include their excellent cold workability

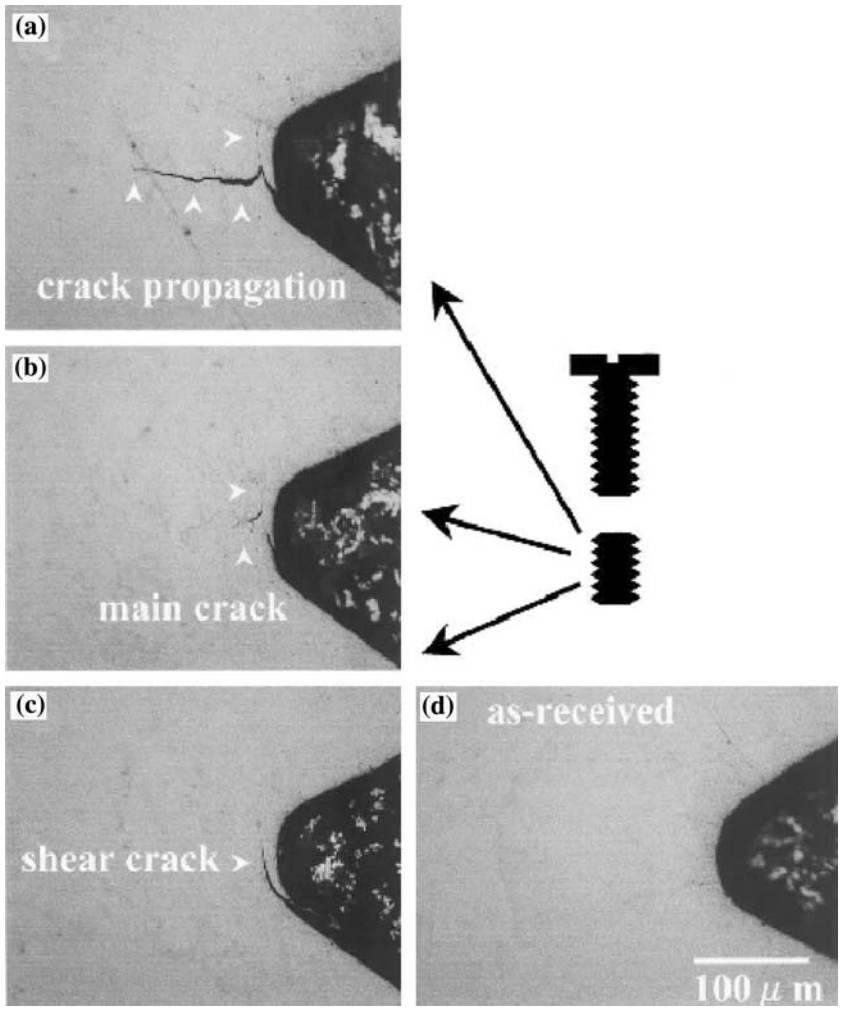


Fig. 4 Fracture failure of Ti–6Al–4V dental screw [79]

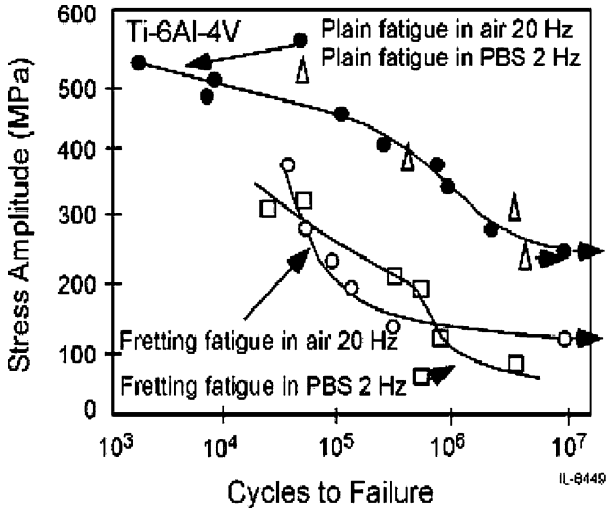


Fig. 5 Fretting fatigue of Ti–6Al–4V in phosphate buffer solution [36]

and high strength. Alloys containing niobium such as Ti–6Al–4Nb showed better corrosion resistance than Ti–6Al–4V with comparable mechanical properties [197, 198]. Titanium alloys containing niobium and zirconium (Ti–13Nb–13Zr) are reported to be the most corrosion resistant followed by Ti–6Al–4V during corrosion and wear-accelerated corrosion tests in phosphate buffer solutions [191]. The increase in corrosion resistance of titanium with the addition of Nb and Zr is due to the fact that they are less soluble in titanium than Al and V and their oxides are more inert (than the oxides of Al and V) resulting in higher film corrosion resistance [191].

The corrosion resistance of various Ti alloys in phosphate buffer solution expressed in terms of E_b–E_p (the difference of break down and repassivation potentials) is presented in Fig. 6 [191]. The lower the difference between two potentials (E_b-E_p) the more corrosion resistant is the alloy. However, these alloys behave differently with addition of protein or change in pH (to simulate the body fluid conditions) of the phosphate buffer solution. The protein addition was found to have favorable effects on corrosion resistance of Ti–6Al–4V whereas it reduced the corrosion resistance of other two alloys (Ti–13Nb–13Zr and Ti–6Al–7Nb) [192]. Increase in pH of the phosphate buffer solution reduced the corrosion resistance of Ti–6Al–4V and Ti–6Al–7Nb whereas it increased it for Ti–13Nb–13Zr [186].

The effects of wear debris generated from Ti–6Al–4V and Ti–6Al–6Nb on cellular behavior has been investigated in a in-vitro study [198]. A large increase in prostaglandin E2 (PGE2) release in the presence of Ti–6Al–4V compared to in the presence of Ti–6Al–6Nb and Ti–13Nb–13Zr was observed and the release of other inflammatory cytokines in the presence of Ti–6Al–4V was also reported [196]. These results indicated that Ti–6Al–4V stimulates phagocytic cells more than Ti–6Al–6Nb or Ti. A release of increasing quantity of pro-inflammatory and osteolytic mediators by the bone marrow cell culture due to the presence of Ti–6Al–4V has been responsible for aseptic loosening of the prosthesis [199]. In another study, a titanium–niobium–nitride surface showed the greatest proliferation of the human foetal osteoblast [200]. Furthermore, the zirconium and niobium containing titanium alloys seem to be more promising as the corrosion products (containing niobium and zirconium) from such alloys are less soluble than that from Ti–6Al–4V. Also, the passive oxide layer on the surface of the former is more inert, consisting of a dense rutile structure that provides greater protection to the underlying alloy [201, 202].

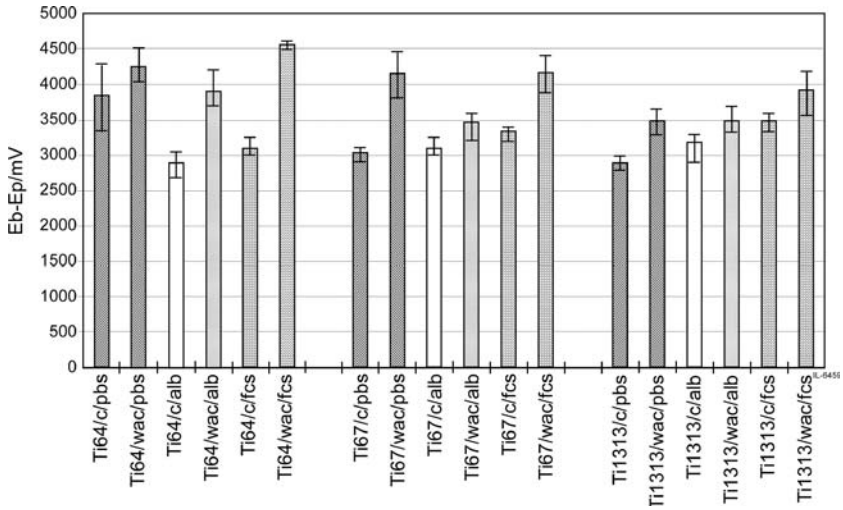


Fig. 6 E_b–E_p for three Ti-alloys in phosphate buffered saline, 1 mg/mL bovine albumin or 10% foetal calf serum under conditions of corrosion or wear-accelerated corrosion presented as the mean and the range of three measurements. Ti64 = Ti–6Al–4V, Ti67 = Ti–6Al–7Nb, Ti1313 = Ti–13Nb–13Zr, c = corrosion, wac = wear-accelerated corrosion, pbs = phosphate buffered saline, alb = 1 mg/mL bovine albumin, fcs-10% foetal calf serum [191]

The deliberate porosity produced on the surface of titanium and titanium alloys to provide better anchorage for growing bone tissues is another area of research [203]. Such growth of the bone tissues enables the stresses to be transferred from the implant to the bone. However, the advantages of these alloys are offset by the tendency of pores to suffer from localized corrosion such as pitting and crevice. Porous titanium was found to be more susceptible to corrosion than solid titanium and SS316L [203].

In spite of the good corrosion resistance and biocompatibility of titanium, its softness and low wear resistance restrict its use in sliding surfaces [204]. Tissue blackening around the titanium hip implant indicates the wear of titanium alloys. This additionally causes a tissue reaction and subsequent osteolysis [205]. Diamond coating and other surface modification strategies have been shown to improve the wear resistance of titanium and titanium alloys [206]. Pin-on-disc experiments using diamond coated Ti–6Al–4V disc against semi-spherical pin made from diamond coated Ti–6Al–4V, uncoated Ti–6Al–4V, SS316L, and Co–Cr alloy have shown significantly low wear rates and low coefficients of friction in Ringer's and synthetic serum (plasmion) solutions. The final wear rate of various pins against diamond coated Ti–6Al–4V disc in different environments is illustrated in Fig. 7 [206].

2.3 Co–Cr alloys

Co–Cr–Mo alloy (Co-64, Cr-29, Mo-6, Fe-0.02, Ni-0.02, all in wt%) is currently an important orthopaedic alloy. It is characterized by superior strength, wear resistance, hardness, and adequate corrosion resistance and is therefore, the metal of choice for articulating surfaces of hip and knee joint replacements [31]. The electrochemical investigations on Co–Cr alloy are scarce when compared to that of stainless steel and titanium/titanium alloys. Chromium and molybdenum in the alloy enhance its corrosion resistance by forming protective cobalt mixed chromium oxide layer. A wide passivation range from –300 to +600 mV (with respect to SCE) and no active-passive transition during anodic polarization of Co–Cr in Hank's solution has been reported [207]. Under mechanical load and electrochemical potential (in the passive region), the corrosion resistance of Co–Cr and Ti–6Al–4V oxide layers were compared [208]. The oxide film on Co–Cr alloy was more resistant to fracture and had a higher interfacial strength than the film on Ti–6Al–4V. However, when the film was not mechanically disturbed (without scratch), the titanium alloy showed better resistance under a wide potential range. Figures 8(a) and (b) [208] showed higher peak current for Ti-alloy than for Co–Cr after scratching the passive layer. However, the similar scratching experiments on Co–Cr–Mo and Ti–6Al–4V alloy coated with TiN/AlN indicated further improvement in the oxide film resistance as seen in Figs. 9(a) and (b) [208]. The TiN and AlN coatings on both Co–Cr–Mo and Ti–6Al–4V showed better corrosion and fretting resistance and higher hardness. A corrosion study on Co–Cr–Mo alloy in 0.15 M NaCl solution using electrochemical impedance technique showed it to have a high corrosion resistance [209]. Spontaneous formation of a protective

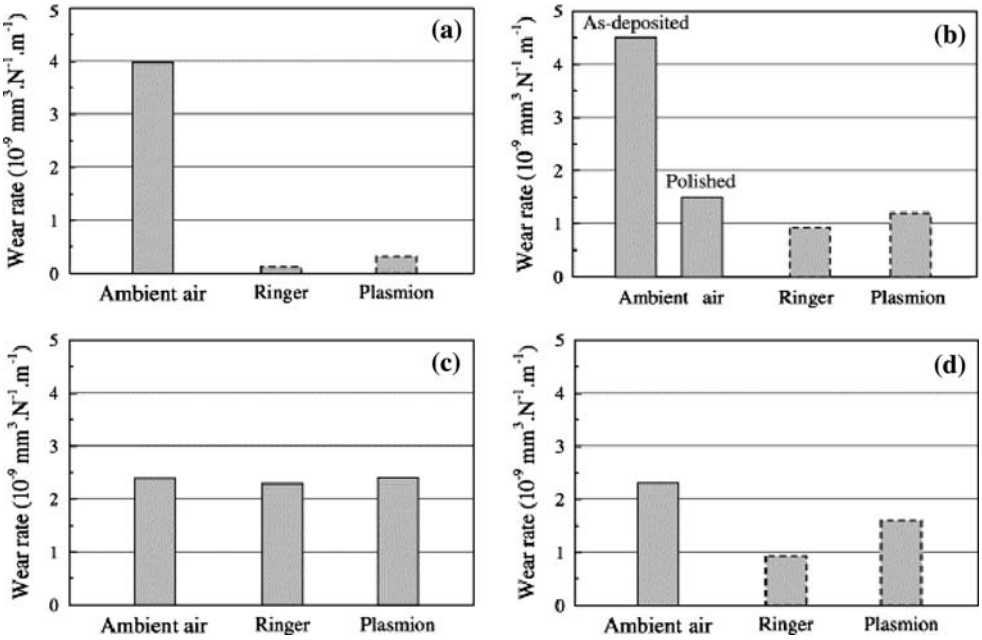


Fig. 7 Final wear rate in different environments for 8 km sliding distance at speed of 0.1 m/s and normal load of 13N (**a**) diamond coated Ti–6Al–4V, (**b**) uncoated Ti–6Al–4V, (**c**) SS316L, and (d) Co–28Cr–6Mo alloy pin [206]

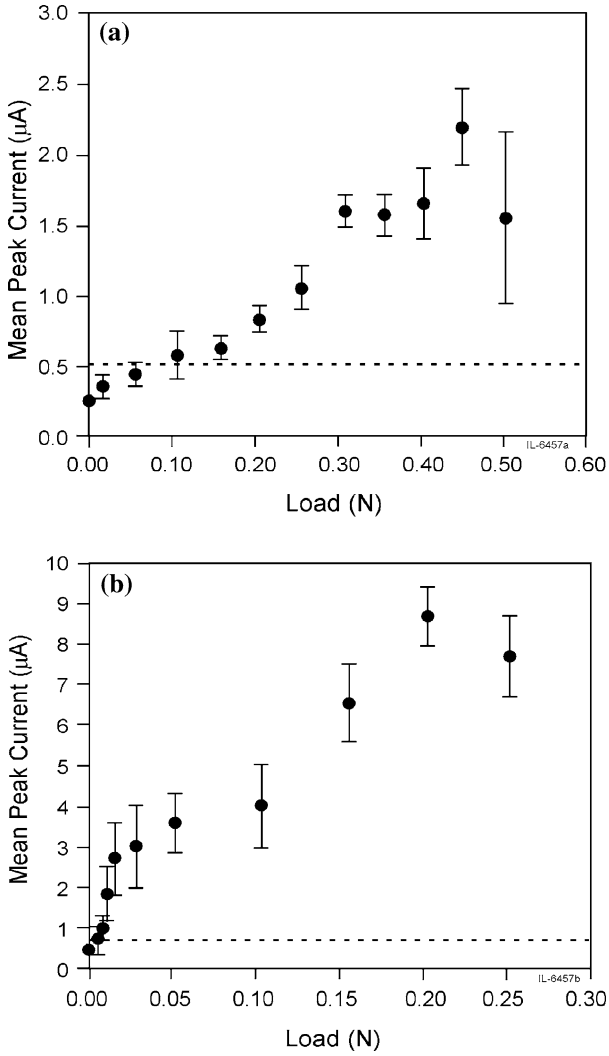


Fig. 8 Mean peak current versus load for passivated and scratched (**a**) Co–Cr–Mo and (**b**) Ti–6Al–4V. All scratches were 50 μm long and made at a constant potential of +200 mV (versus Ag/AgCl). Dotted line indicates background noise [208]

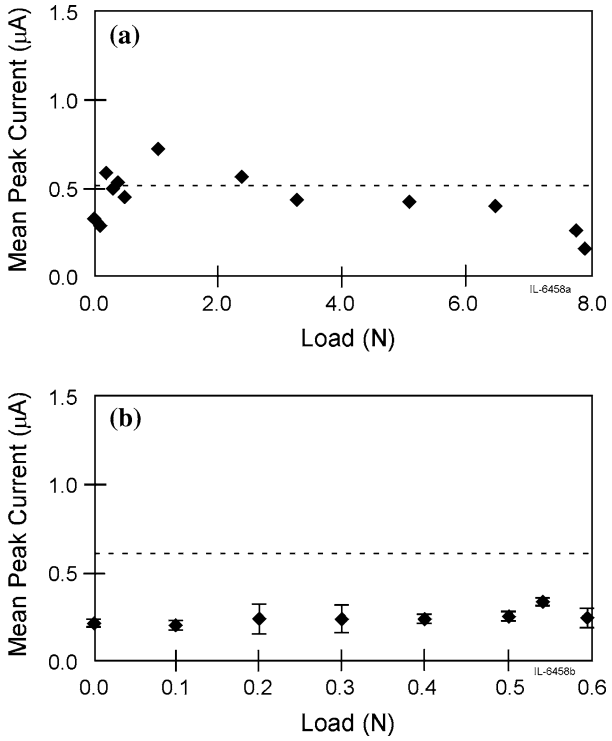


Fig. 9 Mean peak current versus load of passivated and scratched TiN/AlN coated (**a**) Co–Cr–Mo and (**b**) Ti–6Al–4V. All scratches were 50 μm long and were made at a constant potential of +200 mV (versus Ag/AgCl). Dotted line indicates background noise [208]

surface layer on the Co–Cr alloy was responsible for its corrosion resistance [209]. Heat and nitric acid treatments increased the thickness of surface oxide with higher concentrations of oxygen and chromium that, in turn, appeared to be good for the anti-corrosion properties of the film [210, 211].

Several works have been devoted to study surface oxide chemistry of Co–Cr alloy, produced under different conditions [212–224]. These studies were based on techniques such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and Surface Enhanced Raman (SER) spectroscopy [207, 221–224]. The passive film on Co–Cr was reported to depend on the electric potential. A film of 3.1 nm thickness formed on Co–Cr alloy in Hank's solution was found to consist of Cr_2O_3 and $Cr(OH)_3$ at lower anodic potentials (in the passive range) [207]. However, in addition to the above compounds, CoO and MoO_3 were also present at higher polarization potentials and were accompanied by an increase in the film thickness. The addition of a complexing agent such as sodium citrate (a component of the physiological solution) to Hank's solution was reported to affect passive film behavior [207]. Hanawa et al. [221] have characterized the surface oxide on Co–Cr–Mo alloys immersed in Hank's solution, immersed in a cell culture medium (Eagles MEM containing 10% fetal bovine serum FBS in the incubator), and incubated with cultured cell, L929 respectively [221]. The characterization of these oxide layers was done after polishing in de-ionized water. The surface oxide was found to be >2.5 nm thick (in all cases), and was highly hydrated with large amounts of OH^-. The presence of cobalt was observed in the oxide film developed after polishing in de-ionized water. Cobalt was, however, absent in the oxide film that developed in the Hank's solution and only Cr (III)-oxide and Mo-oxide were the part of passive film there. The elements observed in the oxide film formed on Co–Cr after treatments in various media are listed in Table 7 [221]. Study

Table 7 Composition and thickness (t) of surface oxide films after treating Co–Cr alloy in various media [221]

Medium	Elements (wt%)									
	Co	Cr	Mo	O	Ca	P	Na	Cl	Co/Cr	t (μm)
Polished	11	10	1.1	78	0	0	0	0	1.03	2.5
Autoclaved	11	13	0.9	76	0	0	0	0	0.84	2.9
Hank	0	18	1	77	1.2	1.7	0.9	0.4	0	2.6
MEM + FBS	0	9.6	1.1	85	1.4	1.1	1.2	0.9	0	2.8
L929	0	8.7	0.7	90	0.1	0.8	0	0	0	2.5

suggested that the preferential dissolution of the cobalt occurred and that it dissolved in body fluid, however, chromium and molybdenum remained in the oxide films. Calcium phosphate was also found to be a part of the surface developed in Hank's solution with a Ca/P ratio equal to 0.7. The ratio was smaller than that found on the titanium alloys (~1.3) [223].

In a study aiming at the influence of corrosion products on toxicity, Co–Cr was found to be more toxic than that of SS316L with regard to the product formed during corrosion reactions [225, 226]. Cr, Ni, and Co are all toxic elements to living tissues. The presence of albumin, however, decreases the metal toxicity, possibly by chelating the metal ions and forming non-toxic products [225]. Under the physiological conditions, the toxicity of Co and Cr from Co–Cr alloys or Fe from SS316L is reduced with the age but they may produce more bone resorbing mediators [226].

The low ductility of Co–Cr alloys remains a problem and significant research has been going on in this area. Efforts are also made to improve its properties by adding varying amounts of nickel and molybdenum. Addition of chromium was good for increasing hardness where as nickel found to reduce the hardness. While optimizing the corrosion resistance as well as mechanical properties, it was found that ternary Co–Cr–Ni has a larger region in the phase diagram where good properties for biomedical applications can be achieved. This region was relatively smaller for Co–Cr–Mo alloys [227]. Alloys such as $Co_{60}Cr_{30}Ni_{10}$ and $Co_{55}Cr_{40}Ni_5$ are among the 10 studied compositions that were found to have dendritic microstructure useful for dental applications. These alloys possess hardnesses of 257 and 296 MPa (Hv) respectively with significant corrosion resistance. Table 8 [227] lists hardness and break down potentials (pitting potential) for Co–Cr alloys after alloying with varied amounts of Mo and Ni. $Co_{60}Cr_{30}Ni_{10}$ is close to the commercial Co–Cr dental alloy. However, the latter is harder with hardnesses up to 350 MPa (Hv). Investigation of variation in properties such as hardness, microstructure, and corrosion with the change in composition of Co–Cr alloys may provide some understanding for future developments of these alloys.

Table 8 Hardness and pitting potentials of Co–Cr alloys with different Ni and Mo compositions [227]

Composition	Pitting potential, mV (SCE)	Hardness, MPa (Hv) (30N,10 s)
$Co_{55}Cr_5Ni_{40}$	+20	100
$Co_{72.5}Cr_5Ni_{22.5}$	+40	201
$Co_{90}Cr_5Ni_5$	–18	182
$Co_{72.5}Cr_{22.5}Ni_5$	+300	232
$Co_{55}Cr_{40}Ni_5$.	+990	296
$Co_{55}Cr_{22.5}Ni_{22.5}$	+405	201
$Co_{60}Cr_{10}Ni_{30}$	+65	121
$Co_{80}Cr_{10}Ni_{10}$	+60	203
$Co_{60}Cr_{30}Ni_{10}$	+930	257
$Co_{67}Cr_{16.5}Ni_{16}$	+180	201
$Co_{55}Cr_5Mo_{40}$	+160	–
$Co_{75}Cr_5Mo_{20}$	+270	–
$Co_{90}Cr_5Mo_5$	–70	–
$Co_{75}Cr_{20}Mo_5$	+940	–
$Co_{55}Cr_{40}Mo_5$	+920	–
$Co_{55}Cr_{20}Mo_{25}$	+910	–
$Co_{60}Cr_{10}Mo_{30}$	+520	–
$Co_{80}Cr_{10}Mo_{10}$	+740	–
$Co_{60}Cr_{30}Mo_{10}$	+1050	–
$Co_{75}Cr_{12.5}Mo_{12.5}$	+935	–

2.4 Ni–Ti shape memory alloys

The Ni–Ti (nitinol) alloys are interesting medical alloys for several in-vivo applications. These alloys are popular due to their shape memory and superelasticity (pseudoelasticity) effects. The shape memory effect involves the recovery of deformation induced at low temperature. The controlled shape change is obtained when heated up to certain temperature and strains up to 8% can be recovered. This alloy transforms between the martensite phase (stable at low temperature and high stresses) and an austenite phase (stable at high temperature and low stresses). The transformation from austenite to martensite can be accomplished by lowering the temperature through the martensite start (M_s) and martensite finish (M_f) transformation

temperatures. The transformation from martensite to austenite can be induced by heating through the austenite start (A_s) to austenite finish (A_f) temperatures [228]. The austenite can also be transformed by increasing loading stresses at temperatures above A_f temperature. At an appropriate temperature, Ni–Ti alloys are pseudoelastic, meaning they can undergo pseudoelastic transformations that allow the materials to absorb large stains before permanent changes occur. This alloy is used as wire for orthodontic tooth alignment, medical guide wires for diagnostic and therapeutic catheters, osteosynthesis staples, and cardiovascular applications [228–230].

The good corrosion behavior of Ni–Ti alloy is due to the impermeable TiO_2 passive film, which may act as a barrier to nickel ion release [231, 232]. The passive layer on Ni–Ti alloy has been shown to consist of carbide particles in addition to TiO_2 that destabilize the film and could be sites for pitting corrosion [231, 232]. Carbide particles are most likely to enter from the graphite crucible used during the melting process. Several studies have been conducted to investigate the pitting resistance of Ni–Ti alloy [229–231, 233–239]. The pitting potential (using potentiodynamic method) of Ni–Ti was reported to be higher than +1200 mV. This further indicates that the localized corrosion resistance of Ni–Ti alloy is similar to Ti–6Al–4V [233, 234]. However; the tests conducted according to ASTM F746 showed the pitting resistance of Ni-Ti alloy to be much below that of Ti-6Al-4V. The pitting resistance of some alloys is shown in the following decreasing order [233].

$$\mathrm{Ti-6Al-4V} >> \mathrm{ASTM\ F138} > \mathrm{SS316} > \mathrm{Ni-Ti} - \mathrm{Fe} > \mathrm{Ni-Ti} \quad (3)$$

In presence of cysteine amino acid (present in the biofluid), Ni–Ti showed a marked reduction in the pitting potential whereas it did not affect the pitting of Ti–6A1–4V [234].

Several other researchers believe that Ni-Ti possesses a low pitting resistance, though better than stainless steels [229, 235, 236]. In 0.9 wt% NaCl solution, Ni–Ti was compared with stainless steel and Co–Cr alloys and found to be similar to that of the stainless steel. It has been advocated that both stainless steel and Ni–Ti alloy are susceptible to pitting corrosion in saline solutions (simulated to body fluid) [222]. The OCP of titanium and stainless steels in in-vivo are recorded to be about +450 to +550 mV and +200 to +350 mV (SCE), respectively [236]. Since the latter value is close to the pitting potential of both stainless steel and Ni–Ti (in saline solution), pitting corrosion is likely to occur. Ni–Ti, however, can be safely considered for use in the saliva-like environment (as saliva is less corrosive than the saline or Hank's/Ringer's solution) where it has exhibited pitting potential equal to the pitting potential of Co–Cr. Therefore, Ni–Ti can be used for orthodontic wire. A similar conclusion was made when four orthodontic wires in a chloride-induced corrosion test were compared [237]. Wever et al. [229] showed the superiority of Ni–Ti alloy over stainless steel 316LVM, which was due to the formation of a TiO_2 protective passive film in Hank's solution at 37°C. This is apparent from the anodic polarization behavior shown in Fig. 10 [229, 230]. According to few studies, even though Ni–Ti displayed a satisfactory passive range during in-vivo and in-vitro potentiodynamic tests, it exhibited an unstable pitting potential [238, 239]. This was due to variable passive film properties that affect long term performance for clinical applications.

In-vitro corrosion studies of Ni-Ti alloys were conducted and compared with pure nickel, pure titanium (its constituents), and SS316L in three different media: artificial saliva, a cultural medium known as RPMI complemented with 10% foetal calf serum (FCS), and a cultural medium in combination with CEM human lymphoid cell line [239]. Pure nickel was highly susceptible to corrosion where the rest showed significant resistance (Ti–6Al–4V ≥ Ti > Ni–Ti > SS316L > Ni) in all of the tested media. The electrochemical parameters of Ni-Ti with some other biometallic materials obtained in various biofluid media are presented in Table 9 [240].

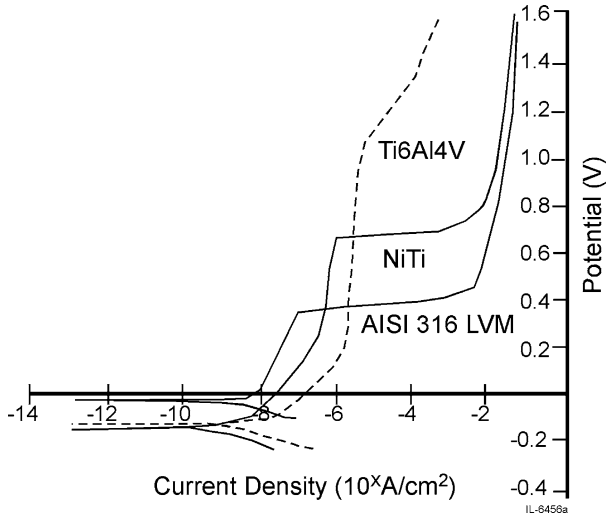


Fig. 10 Electrochemical polarization curves of SS316L, Ni–Ti and Ti–6Al–4V in Hank's solution at 37°C [229, 230]

Table 9 Electrochemical parameters of some biomaterials in different simulated biofluid (potentials are reported with respect to Ag/AgCl electrode) [240]

Biomaterials and Biofluids	E_a, mV	E_c, mV	E_r, mV	I_p(at 400 mV /SCE), μa
Ni in (art. saliva))	–650	–500	–200	13,000
In RPMI	–412	–287	+9	15,300
In RPMI + CEM	–347	–282	+2	8000
Ti in (art. saliva))	–350	<+800	>+1000	5
In RPMI	–145	–416	> +1000	2
In RPMI + CEM	–121	–287	> +1000	3
Ni-Ti in (art. saliva))	–322	–730	+1000	19.4
In RPMI	–338	–425	+600	44
In RPMI + CEM	–352	–615	+530	56
Ti-6Al-4V in (art. saliva))	–328	–600	> +1000	2
In RPMI	–274	–454	> +1000	2
In RPMI + CEM	–109	–454	> +1000	3
SS316L in (art. saliva)	–290	–650	+300	160
In RPMI	–341	–450	+280	5300
In RPMI + CEM	–386	–400	+150	42,600

E_a: rest potential, E_c: corrosion potential, E_r: breakdown potential, I_p: passive current.

The corrosion resistance of porous Ni–Ti alloy in physiological Hank's solution has been reported to be less than that of solid Ni–Ti [241, 242]. Porous biomaterials are considered good for growth of bone tissues, fluid transportation, and improved fixation strength. In Hank's solution, the pitting potential of porous Ni–Ti was about +277 mV while for solid Ni–Ti it was +648 mV. The formation of crevices, hence a more corrosive solution within the pores, could be a reason for the lowering of localized corrosion resistance in the porous Ni–Ti. Furthermore, the effect of strain on the corrosion performance of Ni–Ti alloys have also been investigated [243]. Cold work seems to improve the corrosion resistance of Ni–Ti in the cold drawn and deformed state after annealing. After deforming annealed Ni–Ti by 76%, it exhibited breakdown potentials greater than +1000 mV and current densities lower than 10 μA/cm2 in Ringer's solution.

The biocompatibility of Ni–Ti alloys is still a subject of controversy [240–249]. The presence of nickel in Ni–Ti did not cause cytotoxic reaction, and physiological and cell behavior remained unchanged [240]. In-vitro study by Ryhanen et al. [245] indicated the absence of toxic effects and no decrease in cell proliferation when using Ni–Ti alloys. Shabalovskaya [246] has stated that in-vivo use of Ni–Ti for more than a decade did not show any onset of allergic reactions. Additionally, no corrosion attacks were found on the implants and hence no traces of alloy constituents were found in the surrounding tissues. The general conclusion of their work was that the biocompatibility of Ni–Ti alloys is similar to that of Co–Cr and stainless steel alloys. The additional in-vivo studies also confirmed the biocompatibility of Ni–Ti alloys to be similar to that of the titanium, Co–Cr, and stainless steel alloys [247–249]. During in-vitro studies in saliva, Barret et al. [249] and Bishara et al. [250] found that Ni–Ti components released an average of 13.05 mg/day of Ni, which is significantly below the estimated average dietary intake of 200–300 mg/day. However, Ni–Ti has also shown evidence of cytotoxic reactions in the body [251]. The precipitated corrosion products from a nitinol stent wire were toxic to the vascular muscle cells, especially when the concentration of released nickel was over 9 ppm [252].

3 Corrosion mitigation in biomaterials by surface modification

Surface modification and use of highly corrosion resistant alloys are the most viable options for increasing the corrosion resistance of biomaterial surfaces. Other available methods such as inhibitors, cathodic protection, anodic protection, and the combination thereof may not be feasible in an extremely sensitive and complex bio system. Surface modification has several advantages over designing of highly corrosion resistant alloys. Desirable surface properties can be achieved while preserving the useful properties of the bulk material and therefore reducing the cost of the material. High corrosion and wear resistance, better biocompatibility, increased bone anchorage, and improved aesthetic properties are among a few properties desired for suitable biomedical alloys and can be achieved through surface modification. Along with conventional coating methods, advanced surface modification methods such as plasma-based (plasma ion

implantation, plasma source ion implantation (PSII)), laser melting (LSM), laser alloying (LSA), ion beam, and physical vapor deposition (PVD) have been widely applied to biomaterials. Thermal oxidation and various electrochemical oxidation methods have also been employed to obtain the desired biomaterial surfaces. These methods offer numerous advantages over conventional techniques that include but are not limited to, better interfacial bonding, non-equilibrium phases, faster processing speed, and reduced pollution. However, each of these methods also has some limitations. Some of the widely applied methods for biomaterials are described in the following subsections.

3.1 Plasma-based surface modifications

Plasma based surface modification has been extensively used to enhance tribological performance, corrosion resistance, wettability, adhesion, dyeability, refractive index, and lubricity of biomaterials. The scope of plasma ion implantation extends to the following features:

(i) blood-compatible surfaces (vascular grafts, catheters, stents, heart-valves, membranes for hemodialysis, filters for blood cell separation, biomolecules immobilized on surfaces).
(ii) non-fouling surfaces (intraoculars, contact lenses, wound healing, catheters, biosensors).
(iii) tissue engineering and cell culture (cell growth, antibody production, vascular grafts).
(iv) sterilization of surgical tools and devices (cutting tools of surgeon, tweezers).
(v) biosensors (biomolecules immobilized on surfaces).
(vi) barrier coatings (drug-release, gas-exchange membranes, device protection, corrosion protection, reduction of leaches additives, catalysts, plasticizers).

Plasma ion implantation and plasma immersion ion implantation (PIII) have been employed for stainless steel 316 [253–260], titanium and titanium alloys [261–268], and Ni–Ti [269–275] shape memory alloys. Improvement in wear resistance, while keeping the corrosion resistance intact, is observed for stainless steels treated by plasma immersion ion implantation (PIII) at 400°C that was reportedly due to the formation of expanded austenite [257]. However, further improvement in wear properties after PIII treatment at 500°C was noticed with marked reduction in corrosion resistance due to the transformation of expanded austenite into the CrN phase. Plasma ion implantation at higher temperatures causes the loss of chromium from the solid solution and the formation of the chromium nitride phase that has poor corrosion resistance. Others have observed that plasma nitriding can enhance the plain fatigue and fretting fatigue limit of SS316 [258]. Nitrogen ion implantation on titanium coated (by thermal evaporation) stainless steels has improved its corrosion behavior in 0.5 N H_2SO_4 and 0.5 N HNO_3 solutions [10]. The corrosion resistance is reported to saturate after reaching certain N_2 levels during plasma ion implantation. The low energy plasma ion immersion has indicated a very high pitting potential of stainless steel in Ringer's solutions at pH ~7.2 and 3.5 at 37°C. The improvement was due to a nitrogen rich (32%N) phase (γ_N) in stainless steels, which has been recommended for biomedical applications [260]. Figure 11 shows the effect of plasma source ion nitriding on the electrochemical polarization

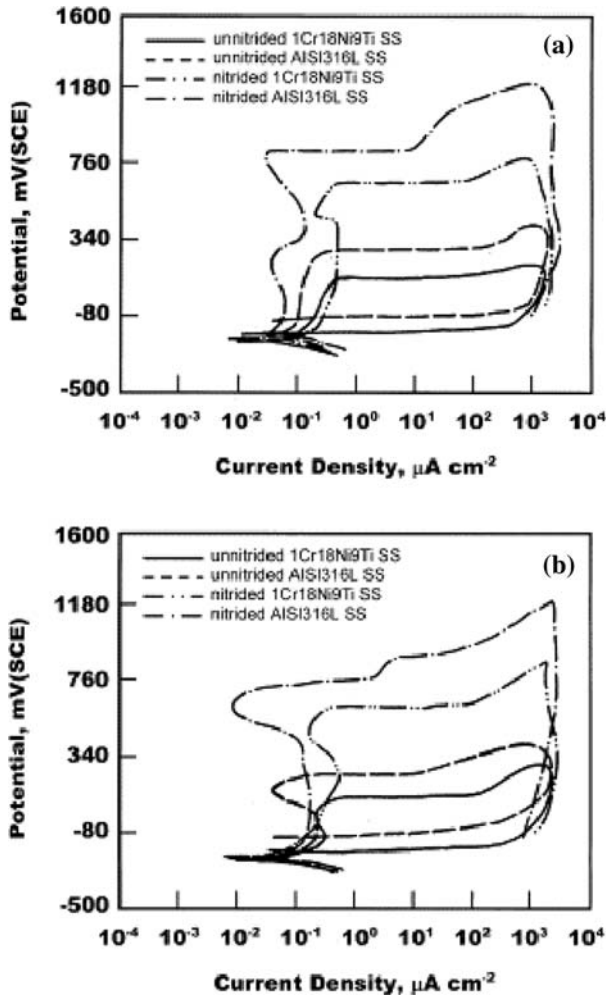


Fig. 11 The electrochemical polarization of stainless steels before and after plasma source ion nitriding in Ringer's solution at (**a**) pH~7.2 and (**b**) pH~5.5 at 37°C [260]

behaviors of stainless steels in Ringer's solution of pH ~ 7.2 and 5.5 at 37°C [260].

Surface modification of titanium and titanium alloys has been carried out to improve their wear and corrosion resistance properties [261–268]. The effect of nitrogen-ion implantation and plasma nitriding has been shown to be either beneficial or detrimental to the fatigue resistance of titanium alloys [261]. The wear and corrosion resistance depends on treatment conditions. Plasma nitriding over short times produced an improvement, whereas longer process times was detrimental to the corrosion fatigue properties [261]. The nitrogen ion implanted surfaces had better corrosion resistance than the pulsed-plasma nitrided surfaces [262]. The nitriding of titanium/Ti-alloy surfaces has been extensively studied for wear and corrosion resistance [263–265]. The corrosion resistance of Ti–6Al–7Nb alloys has been found to increase after both nitrogen ion implantation and pulsed-plasma nitriding. The current density of Ti–6Al–7Nb during passivation was significantly lowered and had enhanced repassivation. The breakdown potential of the film decreased with an increase in the nitrogen dosage [266].

The effects of ion implantation of various elements, such as C, N, O, Y, Hf, Pd, Ir Pt, and Au, on the electrochemical behavior of Ti–6Al–4V in Ringer's solution have been investigated [266]. The specimens implanted with carbon monoxide, carbon dioxide, hafnium, and noble metals possessed improved passivation while the implantation of carbon, nitrogen and yitrium led to a reduction in the passivation properties [266]. TiC appeared to be more harmful than the TiN in terms of reducing the breakdown potential [266]. Calcium and phosphorous ions were also implanted to enhance the biocompatibility and corrosion resistance of titanium [267, 268]. The surface layer of titanium after calcium ion implantation was composed of amorphous TiO_2; Ti_2O_3; CaO; and $Ca(OH)_2$. The electrochemical polarization behavior indicated that the calcium ion implantation at a dose of 1×10^{17} ions/cm^2 increased the corrosion resistance under stationary conditions (conducted at E_{corr} using electrode impedance spectroscopy, EIS), however it experienced pitting at high potentials during potentiodynamic anodic polarization in simulated body fluid. Furthermore, both the non-treated as well as the calcium ion implanted titanium surfaces confirmed the biocompatibility during the in-vitro studies [267]. Phosphorous ion implantation at the same dose rate produced an amorphous surface, which increased the pitting resistance during short as well as long-term polarization experiments in simulated body fluids at 37°C [268].

The pitting corrosion and wear resistance of austenitic Ni–Ti alloys, that have undergone different heat treatments to induce pseudoelastic properties, have been investigated after oxygen ion implantation (at a dose rate of 5×10^{16}, 1×10^{17}, and 3×10^{17} ions/cm^2). Both the ion implantation and heat treatment influenced the corrosion behavior of Ni–Ti in Hank's solution. The highest pitting resistance was for Ni–Ti (equi-atomic) treated at the A_f (austenite finish temperature) 21°C and implanted at a dose of 1×10^{17} ions/cm^2 [269]. The ion-implanted specimens showed higher wear resistance than the heat-treated specimens which could be due to the formation of a $Ti_{11}Ni_{14}$ phase in the subsurface region during ion implantation. Plasma source ion implantation (PSII) is a out-of-line-of-sight surface modification technique capable of dramatically altering the composition of the top 0.1–0.2 μm deep surface material. A graded surface with different functionality can be produced on 50.8Ti–Ni (at%) using plasma source oxygen ion implantation. Such graded surfaces were identified using TEM included a top layer of amorphous TiO_2 followed by crystalline $Ti_4Ni_2O_x$ and $Ti_{11}Ni_{14}$. These surfaces are important from the viewpoint of biocompatibility and corrosion resistance [270].

3.2 Laser surface modification

In recent years, among the various surface modification methods, laser-induced surface modification has gained much attention for achieving the desired properties for medical applications. Owing to several unique features associated with laser treatment, it has emerged as a most desirable technique for enhancement of surface properties. Laser surface modification derives its attractiveness in engineering applications mainly due to:

(i) the formation of a narrow heat-affected zone, leaving the bulk properties unchanged and inducing minimal distortion.
(ii) the refinement and homogenization of the microstructure, leading to enhanced mechanical properties and corrosion resistance.
(iii) the possibility of forming novel surface phases unattainable by other methods because of the non-equilibrium nature of the process (i.e. self-quenching).

The relatively rapid rate of processing, the ease of automation, the ability to operate at atmospheric pressure, and the ability to treat selective areas are additional advantages over other surface modification techniques.

High power CO_2 and Nd-YAG lasers along with excimer lasers have been used to improve the

tribological, corrosion, and surface texture properties of stainless steels, [276–280]. Ti-alloys [281–294], and Ni–Ti alloys [295, 296]. The electrochemical polarization studies [277] of laser melted SS316 at different powers in Ringer's physiological solution at 37°C, showed an improvement in one that was treated with a laser energy of 120W/mm^2. Both the pitting potential and the passivation current showed favorable changes after polishing the top surface layer that contained oxides and surface irregularities [276]. The wear resistance and hardness of both stainless steels and titanium alloys improved after laser surface melting in a nitrogen gas atmosphere (to reinforce dendritic TiN coating) [284, 286]. It was concluded that the useful TiN layer with increasing hardness can be produced with a laser melting treatment in nitrogen gas without incurring a loss of corrosion resistance in 2 M HCl solution. Laser melted Ti–6Al–4V showed a significantly lower passivation current when compared to untreated Ti–6Al–4V in Ringer's solution [276].

The electrochemical polarization experiments have been conducted on the excimer laser modified surfaces of Ti–6Al–4V using argon and nitrogen as shielding gases. The pitting potentials of the untreated, Ar-treated, and N-treated titanium alloys have been found to be +3.51, +5.56, and +4.48 V (SCE) respectively in HCl solutions [288]. The corrosion current was also reduced drastically by as much as seven-fold, after laser treatment. These improvements are considered primarily due to the reduction of solute partitioning effect of Al segregated to the α-phase. The nitrogen-treated specimen had a pitting potential of +100 mV that was lower than that of the argon (Ar)-treated specimen. This is considered to be due to formation of TiN precipitates that act as galvanic cathodes at high corrosion potentials. It is envisioned that by using an excimer laser, better corrosion resistance of surface can be attained [288]. This potential stems from the high absorbability of ultraviolet (UV) laser radiation by metals and the fast cooling rate due to the extremely short pulse duration of excimer laser that produces refined and homogenized microstructure. Badekas [289] observed an increase in the pitting potential of excimer laser surface treated pure titanium in a NaCl solution. The formation of surface cracks was observed. These cracks were probably be due to extensive oxidation of titanium irradiated in the ambient atmosphere [286]. Also, ceramic coatings such as hydroxyapatite and calcium were deposited using a pulse laser deposition technique in order to enhance the bioactivity and corrosion properties of titanium surfaces [291–294].

Laser melting of Ni–Ti, with the aim of biomedical applications, using Nd-YAG laser has demonstrated significant improvement in the corrosion resistance in a 3 wt% NaCl solution [295]. Improvement in Ni–Ti processed in air is probably due to an increased amount of TiO_2 and may also be due to a high Ti/Ni ratio of the outermost surface [295]. The corrosion and passivation currents in Hank's physiological solution decreased by two orders of magnitude after the Ni–Ti alloy was surface melted using an excimer laser [296].

3.3 Electrochemical and thermal treatment

Electrochemical methods for modifying the surfaces of titanium and its alloys have been investigated from the standpoint of bioactivity. However, only a few attempts have been made to study the corrosion performance of post processed alloys [297–207]. The surface of commercially pure titanium was modified by exposing it for a long time in simulated body fluids (SBF) [299]. The oxide film developed on the surface contained calcium phosphate and during subsequent experiments it showed an increase in the corrosion resistance in a SBF solution [299]. The increase of the thickness of oxide layer on the titanium alloy either by thermal oxidation or by electrochemical methods has been reported to decrease the corrosion rate. The quantity of metal ions released due to corrosion reduced with an increase in exposure time [301–303].

Generally, the oxide film formed on Ti and Ti-alloys during anodic oxidation treatment is TiO_2, although its structure and composition is still a controversial issue. The film generated below +20 V was amorphous and had stoichiometric defects where the film produced above +45 V consisted of crystalline anatase and rutile structures [304, 305]. In other work [181], it was found from the Raman spectra that the anatase and rutile might also be formed below +5 V. The oxide film produced in H_2SO_4 solution at various galvanostatic potentials below +20 V was composed of an amorphous TiO_2 outer layer and an intermediate layer of $TiO_x + TiO_2$ [181]. A similar study on the oxidation of titanium surfaces in H_2SO_4 solution at different DC voltages ranging from +90 V to +180 V indicated the formation of anatase and rutile TiO_2 and that they have a good apatite forming ability [302, 306]. The SEM photographs and the thin film X-ray diffraction patterns, shown in Figs. 12 and 13, [306], respectively, illustrate the differences among films formed at various potentials [306]. On subsequent immersion (after being anodically oxidized) in simulated body fluids for three days, apatite was formed on titanium surfaces oxidized at +155 V and +180 V while no apatite was formed on

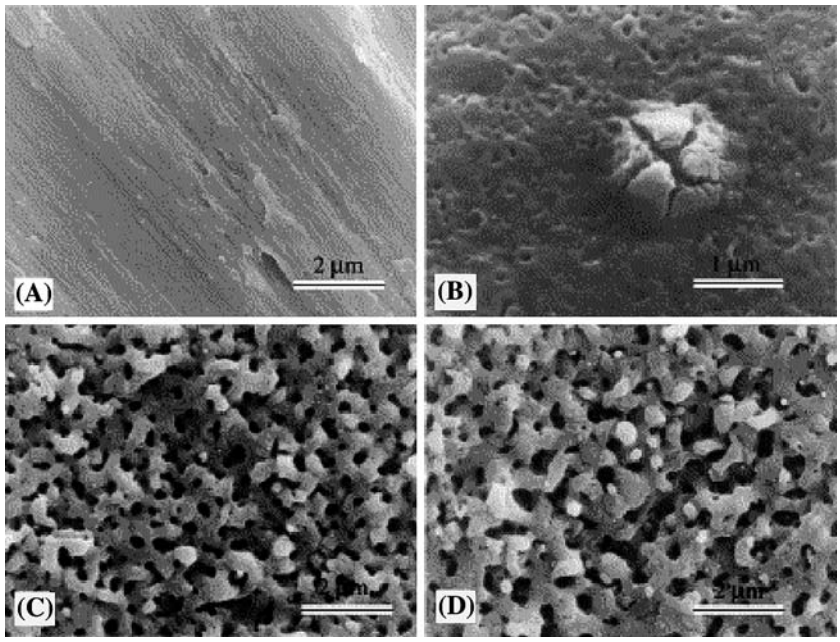


Fig. 12 SEM photographs of (**A**) titanium metal without treatment and anodically oxidized titanium at (**B**) 90 V, (**C**) 155 V, and (**D**) 180 V in 1 M H_2SO_4 for 1 min [306]

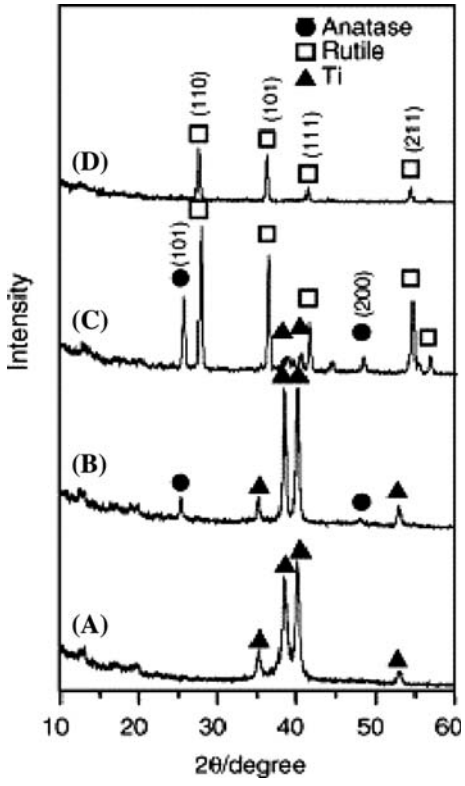


Fig. 13 TF-XRD patterns of (**A**) titanium metals without treatment and titanium metals anodically oxidized at (**B**) 90 V, (**C**) 155 V, and (**D**) 180 V in 1 M H_2SO_4 for 1 min [306]

titanium surfaces oxidized at +90 V [306]. This indicates that a certain amount of titania, of anatase and/or rutile, structures on the oxidized titanium is required for apatite formation. However, the corrosion resistance of such oxidized surfaces (for better bioactivity) needs to be more extensively studied.

Thermal oxidation treatments have also been studied for improved wear and corrosion resistance. In-situ development of a thick and crystalline ceramic rutile film provided improved protection against corrosion in physiological solutions [307–312]. Thermal oxidation of Ti–6Al–4 V was performed at 500 and 700°C for investigation of its corrosion and biocompatibility [307]. During subsequent corrosion studies in Ringer's solutions, the alloy remained unaffected, however, better osteoblastic cell attachment was found for Ti–6Al–4 V that were treated at 700°C. The reduction in metal ion emission from thermally treated when compared to a standard commercially treated titanium hip joint is also reported to be due to the formation of a stable rutile oxide [301, 311].

Other surface modification techniques, such as ion beam assisted deposition (IBAD), chemical vapor deposition (CVD), and physical vapor deposition (PVD); have also been utilized to improve the corrosion performance of biomedical materials. Stainless steel 316L was improved for biomedical purposes by coating with the noble metals Au, Ag, Cu, and Zn using vapor deposition followed by ion beam mixing [313]. Ceramic coating (Al_2O_3) followed by coating with noble metals was produced by ion beam-assisted deposition to avoid galvanic corrosion. Potentiostatic and potentiodynamic polarization studies indicated a variation in the corrosion behavior in physiological

saline solution and human plasma. The coatings with high corrosion protection in human plasma, sometimes had poor corrosion resistance in physiological chloride solutions [313]. A combination of alumina and silver coating offered the best corrosion properties. The coatings produced by CVD and PVD experienced failures in long-term applications [314, 315]. Delamination of TiN coating produced by CVD and PVD on articulating surfaces of Ti-alloy orthopaedic implants has been observed in few in-vitro wear simulations and clinical studies [314, 315]. In addition, TiN coatings contained structural defects such as pinholes. Since TiN coating is nobler to many alloys including stainless steels and Ti, it remains unattacked when exposed to corrosive solutions. However, the substrate exposed to solution through the minute pinholes in the coating experienced rapid corrosion. Generally, CVD and PVD coatings are poorly adhered to the surface due to limited or no interaction between the substrate and deposit, and therefore improvements are required when employing CVD or PVD techniques for coatings.

4 Interdependence of oxides, corrosion, and the host environment

Corrosion resistance of metallic alloys greatly depends on the oxide formed on the surface. Some specific oxides, such as titanium oxide, are also helpful in facilitating tissue and bone in-growth; oxides can also influence the cell/ tissue reaction near implant device [160, 188, 189, 207]. The composition and thickness of the oxide determine the corrosion resistance of the individual alloy/metal, the formation of which is guided by environmental parameters. For example, among various biomaterials, chromium oxides on stainless steels, a mixture of chromium and cobalt oxides on Co–Cr alloys, and titanium oxides (TiO_2 and small amount of TiO and Ti_2O_3) on titanium and titanium alloys are responsible for the corrosion resistance of the respective alloys in biofluids. The tissue and cell reactions in addition to the biofluid also influence the oxide composition and thickness. An examination of Ti implants extracted from patients after 6–8 years showed a marked increase in the thickness of the surface oxide layer [177]. Sundgren et al. [160] reported that the thickness of the oxide, mainly Cr_2O_3 on stainless steel wires, increased when implanted in the body for up to 136 days and the increase in thickness was dependent on the metabolic activity of the tissues. Such changes in oxide thickness were not observed during in-vitro studies, therefore, it is reasonable to assume that it could occur due to reaction with host tissues, cells or metabolic activities. It is supported by the findings that the macrophage cells near implants and in tissues release reactive chemical species (RCS), that include nitric oxide (NO), hydrogen peroxide (H_2O_2) and super oxide (O_2^-). During wound healing/tissue remodeling, these species may alter the composition and thickness of the implant surfaces [316]. Due to the importance of oxide layer to meet biocompatibility and corrosion resistance requirements before implantation in the body, devices are being modified to develop suitable oxides by various methods such as: passivation treatment (such as HNO_3 and H_2O_2); thermal treatment; or electrochemical treatment. Heat and nitric acid passivation treatments of Co–Cr implants, before being implanted, increased the alloy surface oxide thickness and enhanced the O and Cr contents that help in reducing corrosion [211].

5 Future work

Several newly developed alloys, such as nitrogen containing stainless steels, beta titanium alloys and Co–Cr–Ni or Co–Cr–Mo alloys, are being developed as alternate biomaterials. These need to be thoroughly investigated for the biocompatibility of their alloying constituents by conducting long-term corrosion and wear-corrosion experiments. The maximum quantity of metal ions that can be released by existing bio-metallic materials as a result of corrosion and wear-corrosion in the most aggressive bio-environment should be established. Such databases along with the knowledge of the tolerable quantity of individual metal ions, without causing an allergic reaction, by the body will be helpful and can act as a reference document for concerned people. This will further facilitate the selection of suitable materials for implant and, in turn, will reduce the failure of implants and pain to patients.

Changes in the material, such as oxide thickness and composition on metallic implants, continue to occur during long-term, in-vivo exposure unlike the discrete changes encountered in in-vitro experiments. Such changes are due to the influence of metabolic processes, reactions with cells and tissues, and the reactions of biofluids with the surface of the metallic implants. For example, macrophage cells, near implants and in tissues, release reactive chemical species (RCS), including nitric oxide (NO), hydrogen peroxide (H_2O_2) and super oxide (O_2^-) which can alter the composition and thickness of oxide [316] which, in turn, will affect the corrosion behavior of the implant materials. Several complex processes in the host cells and tissues in the body can change the surface of

metallic materials or cause the formation of complex compounds (where released metal ion/debris play a role) that can affect health. Research, especially to explore these issues and correlations with health issues, is yet to go a long way. The interaction of different molecular weight proteins with metal ions leached from the implant and the formation of metallo-proteins are some of such complex processes that need further studies [317].

The reconstruction of passive films on bio-metallic materials (or repassivation) is an important issue in reducing the metal ion release. Scratching of passive oxide layers on implants is possible due to frequent movement, abrasion with the hard tissues, and wear. The sooner the passive film is repaired, the lower the quantity of metal ions released into the body. This issue has to be addressed for every bio-metallic material in more detail, particularly with varying bio-environmental (chemical species) and biomechanical conditions. Furthermore, the data-base of clinical failure of implant devices needs to be encouraged so that it will be a valuable tool for further development of biomaterial research.

Bio-metallic materials have a limited number of coating options for enhancing their corrosion resistance, especially due to restrictions imposed by the issue of biocompatibility. Coatings of ceramics (such as calcium phosphate and hydroxyapatite), bioglass (mixture of silica, alumina, magnesia, calcium oxide; sodium oxide and phosphorous oxides) and thermally and electrochemically generated oxides have been tried in order to enhance the bioactivity of surfaces. The electrochemical behavior of such modified surfaces, however, is not well characterized. The coatings, especially bio-glass, should be made more useful for both improving bioactivity and enhancing the corrosion resistance of surfaces. To minimize the delamination or flaking off of coatings, advance coating processes such laser surface alloying need to be investigated further.

The metallic biomaterials those are used for supporting/temporary devices to fractured bone need to remove by second surgery, after bones/ tissues get healed. Degradable magnesium and its alloys are being looked at as alternative materials to fulfill some of these demands [318–320]. Magnesium is a light-weight metal with an elastic modulus (41–45 Gpa) close to bone is degradable. This can, therefore, replace the materials used for temporary devices and can maintain mechanical integrity of diseased or fractured tissues/ bone for over a time scale of 12–18 weeks till the bone tissue heals. The degradation of magnesium would not pose any threat to the biocompatibility as this is an essential element in the human metabolism and also part of the bone and body fluid. The main drawback, however, associated with magnesium is that it can corrode at much higher rate than required for planned duration. Extensive research work is required to improve its corrosion resistance so that it can be used efficiently (with chemical and mechanical integrity) for designed duration till bone/tissues healed up. Using magnesium alloys, stress-shielding effect that results into bone resorption can also be minimized. Stress shielding occurs due to occurring large difference in the elastic modulus between existing biometallic materials and natural bones [318–320].

6 Summary

Stainless steel 316L, titanium and titanium alloys (Ti–6Al–4V), Co–Cr, and nitinol shape memory alloys are the most frequently used metallic materials for bio-applications. Localized corrosion through pitting, crevice formation, galvanic corrosion, corrosion cracking, corrosion fatigue, fretting corrosion and wear corrosion are the most prevalent corrosion types that cause the bio-implants to fail. Titanium and titanium alloys offer the best corrosion resistance followed by Cr–Co, Ni–Ti, and SS316L alloys. The pitting corrosion of Ni-Ti and SS316L is likely in physiological saline medium, although the latter was found suitable for saliva solutions. On the contrary, Co–Cr and Ti–6Al–4V possess significantly high pitting corrosion resistance in physiological solutions. The biocompatibility of SS316L, Co–Cr, and Ni–Ti alloys is affected by the release of Cr, Co, and Ni ions from these alloys, as a result of corrosion. Even though Ti–6Al–4V releases undesirable vanadium, due to the formation of a uniform and adherent TiO_2 film, it is most commonly used in bio-applications.

Titanium has poor wear and wear-corrosion resistance and can generate wear debris that can cause serious health problems. In order to improve the biocompatibility, corrosion, and wear assisted corrosion of these alloys, efforts have been made to replace the toxic constituents with less hazardous elements in the bulk material. Stainless steels are modified by lowering the nickel content and alloying them with Mn or N. Ti–6Al–4V is modified by replacing V with Nb, Zr or Ta in order to make it more biocompatible and corrosion resistant. A surface modification approach has also been adopted. Among the attempts to modify the surfaces to enhance the corrosion resistance and biocompatibility, plasma- and laser-based (laser surface melting and laser surface alloying), electrochemical

oxidation, and thermal oxidation techniques are considered to hold tremendous promise. Calcium containing bioceramic materials are often used as coating on biometal surfaces to improve their functionality. However, the limitations of material systems and the combination of coatings and coating techniques for bio-applications continue to need further development. The composition and thickness of oxide layers on the surface of bio-metals play a great role in altering the corrosion resistance and biocompatibility of bio metallic materials. Host tissue or cell interaction, in addition to biofluids, also effects the composition and thickness of the surface oxide and vice-versa. However, more research has to be conducted in order to explore these phenomena in detail. Formation of suitable oxides on the surface of implants may enhance corrosion resistance and improve their biocompatibility. The intentionally corrodible magnesium alloys are being looked at as an important class of orthopaedic materials, particularly for temporary/ supporting device, so that the second surgery can be avoided. However, it needs more attention and research with regards to its corrosion resistance enhancement.

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