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**Ion Beam Surface Treatment  
of Biomaterials**

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# **Ion Beam Surface Treatment of Biomaterials**

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## **1 Introduction**

Metals, alloys, ceramics and polymers have found widespread applications in orthopedics and dentistry. The selection is limited to some systems: Ti, Ti alloys, stainless steels, Co alloys, alumina, zirconia, carbon and ultrahigh molecular weight polyethylene [1], for reasons of compromising various requirements. The selection criteria are dictated by two global aspects of biofunctionality and biocompatibility [2]. Ability for load bearing, fracture resistance, modulus of elasticity or fatigue resistance are e.g. some elements of the required biofunctionality, which are reasonably pertinent volume properties of the material. But the interactions that occur when foreign biomaterials come into contact with the biological environment, are of superficial and interfacial nature, and the surface and subsurface properties of the material are the factors that determine such events. A vast majority of complications and failures in clinical use of biomaterials is related to this phenomenon of biocompatibility.

All materials have non-zero corrosion rates. Surface breakdown and particulate wear, fretting, and fatigue debris generated at the articulating interface are additional mechanisms contributing to an enhanced ion release. The ion release gradually destroys the material and its function and may mediate local, remote, and systemic site metabolic, immunologic and carcinogenic processes [3,4]. A low level of ion release could be severe if it continues over long periods of time. Preferential accumulation and enrichment of metallic ions in various organs have been reported [5,6]. There is strong evidence for the connection between the ion release and the

biological consequences, like changes in cell proliferation [7] and extracellular matrix [8], and inhibition of apatite formation [9]. The wear debris appear to be correlated with the osteolysis [10]. Current surgical biomaterials contain more than 35 metals [11]. At least ten metals, including Co, Cr, Ti, Ni, and Pb are considered as chemical carcinom. Ni and Co are important allergens, with Ni allergy being one of the most common hypersensitive responses.

Bioactive materials, e.g. some type of ceramics and glasses [12-17], induce direct bonding to tissues. The bonding rate can be optimized to allow strongly adherent bond to be formed with both hard and soft tissues [13,18]. Of great interest has been the use of bioactive material coatings to impart metallic materials biocompatible [19-22]. An important bioceramic coating is hydroxylapatite. Its deposition, preferably by plasma spray [15,23-26], on porous metal surfaces is used for fixation of orthopedic prostheses. The mechanical strength of the bonded interface even exceeds that of the bone [14,27-30]. But most failures observed [12,31] involve cracking at the coating - metal interface. Porous or fiber coated materials [32,33] follow the same intention. These materials have high specific surface areas with enhanced propensity to produce high release rates of corrosion products.

There are conflicting microstructural and compositional requirements for improving mechanical properties and corrosion resistance. For instance, the corrosion resistance increases with decreased propensity for forming grain boundary carbides, which are preferential sites for intergranular corrosion. But microstructures with carbide free grain boundaries are associated with markedly reduced yield and tensile strength [34]. A minimum chromium concentration of 12 % is required for steel to develop a passive film of chromium oxide necessary for corrosion resistance [35]. A Cr content above 28 % leads to the precipitation of grain boundary chromium carbide ( $\text{Cr}_{23}\text{C}_6$ ) and a chromium depletion in a zone adjacent to the carbides. The chromium depleted zone, acting as anode, encourages a localized intergranular corrosion. Stainless steel 316L is strengthened by cold working to achieve fatigue resistance, but the process reduces ductility [1]. The segregation of interstitial impurities, such as nitrogen, to dislocations is a mechanism to raise the yield stress by pinning dislocations. However, the solid solubility e.g. of nitrogen in iron is limited to a level lower than would be effective. These few examples provide evidence for searching alternatives, and one such strategy is the surface modification to impart additional properties without sacrificing important bulk properties.

Recent experimental results provide indications of molecular and cellular elementary processes that govern the earliest stage and the evolution of the interactions biological environment - biomaterial surface. Variable (in composition, contamination, surface energy and charge, and topography) surfaces produced by different preparative procedures induce variable initial cellulare response [10,36-40]. The surface

characteristics are considered to mediate the biological activity through adsorbed protein films [41,42]. The initial attachment of bone cells to prosthetic materials has been shown to be mediated by the adsorption of vitronectin, a serum glycoprotein [43]. The uptake of  $\text{Ca}^{2+}$  and  $(\text{PO}_4)^{3-}$  ions from the body fluids was seen for passive oxide films on commonly used surgical materials, like Ti, its alloys, and stainless steels [44]. The formation of hydroxylapatite appears to be one essential step in the biomineralization process for tissues to be bonded to foreign materials [13,45,46]. The lack of fundamental knowledges of the interfacial interactions, both on molecular and cellular level, appears to be one obstacle to developing more advanced materials [47].

Ion beam techniques offer beneficial aspects, which may well be significant for studying and processing biomaterials. These are (1) controllable tailoring of surface composition, microstructure, stress state, porosity, topography, (2) no interfacial problem of adherence or thermal mismatch, (3) negligible dimensional and appearance change, (4) no elevated temperature, (5) extended range for solid solubility and atom size mismatch, (6) extremely high quenching rates for forming non-equilibrium phases. The acceptance of ion beam techniques has been demonstrated by successes of the industrial treatment of titanium alloy surgical knee prostheses [48,49].

The present review summarizes reported results on ion beam treatment of metals and alloys with implication for biomedical applications. The focus is placed on evaluation regarding electrochemical behaviour and tribomechanical properties of surfaces brought about by energetic ions. The material science aspect is emphasized. As data on typical biomaterials are very limited, the consideration includes some other metals, alloys and ceramics for better understanding of the underlying principles. The microtexturing [50,51] is not considered.

## 2 Aqueous Corrosion

The ion release from biomaterials into the biological medium is closely related to the corrosion properties of the former. The effects of ion beams on the electrochemical behaviour of metals and alloys have been studied extensively for aerospace and tool materials, and to a lesser extent, and only very recently for biomaterials. All the traditional concepts for the enhancement of aqueous corrosion resistance of metals and alloys can be achieved by ion beam treatment, including 1) corrosion-barrier coating, 2) cathodic reactions, 3) anodic reactions, 4) passivation. New aspects brought about by ion beam processing involve 5) surface charge tailoring, 6) surface microstructure, 7) film adherence, porosity and stress. Results on strengthening the corrosion resistance by ion beam treatment are considered in the following along these lines.

## **2.1 Nitrogen Implantation**

Some metal nitrides, carbides or borides are sparingly soluble in aqueous solutions. The beneficial effects of nitrogen as an alloying element in steels are well known regarding mechanical and corrosion properties. The electrochemical behaviour of nitrogen implanted surfaces has been studied on some surgical and dental materials. Williams and Buchanan [52,53] have tested corrosion and wear resistance of Ti6Al4V implanted with nitrogen. To simulate the working situation of an artificial hip joint, the sample was rotated in a saline solution between two loaded conforming polyethylene pads with the sample surface periodically contacting the solution. The sample was anodically polarized and the resulting corrosion current, a measure of the rate of material removal was measured. The result was spectacular in that the current dropped by some 2-3 orders of magnitude. Similar results were reported also by Dearnaley [54]. It was suggested that the effect originates from a surface hardening which alleviates surface abrasion, thus preventing a damage of the corrosion protective layer. But the surface chemistry and the microstructures seem to interplay. Greenwald et al. [55] compared N and N + O implantation in Ti6Al4V by conducting corrosion test in Ringer's solution at 37 °C. In both cases a marked improvement in corrosion resistance was observed. The corrosion potential of N-only implanted surface was initially identical to that of unimplanted surface and drifted slowly towards the noble value of the N + O implanted surface, indicating a passivating process that occurred upon exposing to the solution. Nitrogen implantation [52,56-68] leads to the formation of fine TiN precipitates (10-150 nm in diameter) and dissolved nitrogen. Epitaxial growth of  $TiN_y$ , was observed on thin Ti films by implanting N [69]. There are data [64,67,70] which suggest that a nitrogen containing TiO film in place of the usual  $TiO_2$  develops on the surface and that oxynitride bonds are present in the implanted layer [58,61,62]. A marvellously improved resistance to standard etchant solutions has been reported for Ti6Al4V implanted with nitrogen[49].

Nitrides of other metals, like Fe, Cr and Al have been identified after N implantation into stainless steels [71-74], hard chromium coatings [75-78], and Al and Al based alloys [79,80] and they all showed resistance to corrosion. The effects that CrN and  $Cr_2N$ , resulted from the implantation of nitrogen into hard Cr coatings, are harder than Cr and the compressive state is created by implanted ions provide a mechanism of closing of microcracks. The improved corrosion resistance appeared to relate to this phenomenon [75-78].

Co-Cr based alloys are traditional standard materials in orthopedics for their extreme hardness and wear resistance. The ion release by corrosion is critical for reason of toxicity and carcinogenic nature of the alloy components (mainly Co, Cr and Ni ions). Nitrogen implantation was shown to be very effective in increasing the corrosion resistance of Co-Cr based alloys [48]. The effect was identified to originate from the formed chromium nitride achieving self passivity at the corrosion potential. A preceding N implantation beneficially affected the gas nitriding [81]. For instance,

25 keV N<sup>+</sup> implantation enhanced the thickness of the nitriding layer on AISI 316 stainless steel by about 40 %.

## 2.2 Noble Metal Implantation

Surface alloying with noble metals allows the corrosion process to be controlled by three basic mechanisms. The first mechanism relies on the enhancement of the cathodic process which is able to produce a mixed corrosion potential being markedly more positive than the critical potential for passivation of the base metal. The catalytically promoted cathodic process provides so ready conditions to passivate the base metal, should the protective layer be damaged. This type of improvement of corrosion resistance has been demonstrated by implantation alloying. Noble metal implants studied so far include Au [82], Pt [83,84], Pd [85,86], Rh [82], and Ir [87,88]. The beneficial aspect of the ion beam alloying appears to be the concentration level and the uniform dispersity which are difficult to achieve in a traditional bulk-alloying process. The active dissolution of Pd implanted titanium in boiling 1 M H<sub>2</sub>SO<sub>4</sub> was found by Hubler et al. [85] to be reduced by about three orders of magnitude. Galvanic couples formed by surface Pd and base Ti resulted in corrosion potential more noble than the critical potential for passivation of Ti. In 20 % H<sub>2</sub>SO<sub>4</sub>, the protective TiO<sub>2</sub> layer dissolves and Ti corrodes actively. Ti surfaces implanted with Pd, as demonstrated by Ensinger and Wolf [89], became passivated in the same solution with negligible corrosion during 80 days. The time limit was given by the thickness of the surface alloy achievable by ion implantation. An unimplanted sample survived hardly some hours. In concentrated saline solutions at high temperatures, Ti and Ti alloys suffer from crevice corrosion [90]. Munn and Wolf [86] reported the powerful resistance of a Pd implanted Ti surface to crevice corrosion. With a moderate ion dose of  $1 \times 10^{16}/\text{cm}^2$  of Pd at 200 keV, a Ti surface has been shown to resist crevice attack in boiling 42 % MgCl<sub>2</sub> for up to 4 weeks. The second mechanism that imparts metals to corrosion resistance relates to the chemical inertness of the noble metal. A coherent noble metal film efficiently protects the less noble metal from dissolution in most aqueous solutions. A typical example for this case is the implantation of Ir in Ti6Al4V that has been studied by Williams et al. [91] and Buchanan et al. [87]. The reported results are relevant regarding two aspects. First, upon exposing to 1 N H<sub>2</sub>SO<sub>4</sub>, the corrosion potential of the implanted surface drifted toward noble potentials, and finally approaching the potential value of a pure Ir electrode. As followed from XPS analysis, an enrichment of Ir at the surface occurred as a result of a selective dissolution of the base metal. Starting from initial peak Ir concentrations of 2.5 and 5.0 at.% the end values after enrichment were as high as 60 and 87 at%. The authors estimated 100 % enrichment is possible. In this case the base Ti alloy owes its improved corrosion resistance to the coating film of Ir, the most corrosion resistant metal known [92]. The Ir enrichment was found to



proceed at a slower rate for pure Ti than for alloy. This was attributed to the slower dissolution of Ti as compared to Ti6Al4V. A preferential dissolution of Ti leading to a surface enrichment of Pd (> 20 %) was observed by Hubler et al. [85] with Pd implanted titanium. For Pt implanted in Ti such an enrichment has been also reported by Appleton et al. [84]. They concluded an ad-atom surface diffusion and agglomeration for Pt to account for the enriched retention and the inhomogeneous distribution observed. Second, Ir is a preferred material for neural sensing and stimulating electrodes. It has the best charge-injection capability of any known material [93,94]. A conventional processing faces difficulties due to the chemical resistance and the brittleness of the element. The charge-injection capability of Ir implanted in Ti alloy after electrochemical enrichment was measured to exceed that of pure Ir. The precise mechanism of the phenomenon is not yet fully understood, but the charge injection is thought to result from the reversible transition of  $\text{IrO}_2$  to  $\text{Ir}_2\text{O}_3$  within the hydrated oxide layer.

An inward transport of the noble metal (resulting in enrichment and persistent retention) during selective dissolution of the base metal in  $\text{H}_2\text{SO}_4$  was reported for Pt implanted Fe [95] and Pd implanted Ti [85]. It was thought that the effect involves an enhanced volume diffusion by defects. The details of the process are not known. The final mechanism refers to the inhibition of the cathodic hydrogen evolution reaction. This type of mechanism is applicable to metals having a great active dissolution and no stable passive surface layer. The overall corrosion rate, being a result of the coupled anodic and cathodic processes, will be determined by the success of suppressing the cathodic reaction. The implantation of Cu and Pb [96] into Fe, elements with great over-potential values for  $\text{H}^+$  ion reduction, has demonstrated this principle. The effect of Pb was greater than that of Cu, as expected from the order of their over-potentials.

### **2.3 Implantation of Passivating Elements**

The aqueous corrosion behaviour of passivating metals and alloys is determined by the physicochemical properties of the passive oxide film formed. The corrosion properties modified by ion implantation are the result of the modification of the oxide film growth. Brown and Mackintosh [97] and Mackintosh et al. [98] observed a thickening of the nonporous barrier type oxide film during anodization of implanted Al. The effect was dependent on the implant nature and was correlated to their mobility. The studies by Baily et al [99] and Towler et al [100] showed that the oxide film is of duplex structure with an additional porous layer interfacing the electrolyte solution. The overall effect of implanted ions depends on the complex mechanisms of ionic migration during film growth process [101]. Towler et al. found that those implanted species (Bi, Sn, Pb, and Tl) capable of producing ions of higher valency than Al enhance the film thickening, while film growth is retarded by ions

of lower valency (Au, Cu, Cr, and Ag). Kr did not show any effect, thus fitting to this order. But, Ce, despite its high valency, had only little effect on film thickening. Results of Venkatraman et al. [79] on Ti and V implantation supported this concept. Another aspect is the doping effect of the implants in the context of the Wagner-Hauffe rules [102]. The normal aqueous passivation generally produces on Al an oxide film of n-type semiconductivity and the corrosion of Al is governed by the interstitial excess  $Al^{3+}$  ion concentration. The latter is involved in an equilibrium with electronic defects for preserving charge neutrality. Doping with ions of higher valency generates excess electrons, leading to a reduction in the interstitial excess  $Al^{3+}$  and so in the ionic transport rate. The improvement in corrosion resistance observed on Al appears to be in reasonable agreement with this interpretation.

The effect of Ta and Ni implantation on the corrosion behaviour of Ti has been studied by Sugizaki et al. [103]. Ta was effective in reducing the overall anodic reaction both in the active and passive regions, while Ni significantly promoting the passivation of Ti. The co-implantation of Ta and Ni was shown to unify efficiently beneficial aspects of both single implants. For 316 L stainless steel, the corrosion and abrasion corrosion resistance to chloride containing body fluids is not sufficient enough for long-lasting orthopedic applications [104]. Substantial improvement in corrosion resistance has been reported [105] by nitrogen and specific ion implantation. An alteration of the corrosion behaviour of 316 L stainless steel was achieved by Ni implantation [106]. In addition to Ni being an efficient passivator, the ion bombardment-induced redistribution of the surface constituents may play a part. Ni was found to collect towards the surface, while Cr enriched at a greater depth inward. A proposed model [107] suggests a flow of solute elements following a flow of radiation-generated interstitials: undersized Ni atoms favor interstitial sites and oversized Cr atoms diffusing away from sinks via vacancy migration.

## **2.4 Localized Corrosion**

The pitting corrosion, a localized corrosion attack phenomenon, is strongly affected by the presence of certain anions. Chloride ions, omnipresent in biological environments, are among the hostile species. The locally increased stress at pit sites enhances fatigue crack formation which in turn amplifying the localized corrosion. In all, this conjoint effect exacerbates the entire surface damaging. Alloying and surface coating are two conventional methods to impart resistance to pitting attack. Often, the concentration level of the alloying elements required in order to be effective, is limited by their solid solubility. The effect of ion implantation on pitting corrosion has been studied on some materials including Fe [108-110], Al [111-125], Ti [85,86], and steel [126-130]. For Fe, the implantation of N and B [108] improved resistance to pitting probably by formation of nitride, boride and stabilized mixed oxides. Nitrogen implantation in Al resulted in decrease in pit size and density which

was correlated with AlN formation [131]. An improvement of pitting corrosion resistance and formation of AlN have been identified in Cu alloyed Al implanted with N [115]. Pd implanted in Ti alloy [86] suppressed efficiently pitting attack which was ascribed to an accelerated passivation by a micro-galvanic coupling. Amorphized material is thermodynamically more energetic and hence reactive. But, lack of defects and grain boundaries, two major sources favouring corrosion reactions, may be beneficial. The enhancement in pitting resistance of stainless steels implanted with P [132] and Al [133,134] has shown evidence for some contributions of ion bombardment generated surface amorphisation. For Al, implants such as Si, Cr, Nb, Mo, Ta, Ti, Zr [111,116-119] improved the pitting behaviour, while Mg and Zn [88] exhibiting detrimental effect. Natishan et al. [111,135] have proposed a model based on surface charge considerations and the  $pH_{pzc}$  of zero charge. Surfaces of sparingly soluble inorganic compounds, like oxides, borides and nitrides undergo in aqueous solutions protonation and deprotonation reactions [136,137] and the surface is charged up at pH deviating from  $pH_{pzc}$ , for which the surface is electrically neutral. At pH lower than the  $pH_{pzc}$ , the surface has a net positive charge and anions, such as chloride are attracted to the oxide film resulting in incorporation into and breakdown of the film. At pH higher than  $pH_{pzc}$  the surface is negatively charged and anion adsorption is inhibited. The model predicts that implanted elements capable of producing oxides with lower  $pH_{pzc}$  can reject anion adsorption, thus reducing localized corrosion attack. Natishan et al. [111,117] have examined this rule for a series of selected implants and found reasonable qualitative agreement. A quantitative correlation has failed due to differences in the surface concentrations reached by ion implantation. The effect of surface concentration has been demonstrated by implantation of Ta in Al at room and liquid nitrogen temperature [80]. A greater Ta concentration collected toward surface for liquid nitrogen implantation correlated with a more positive pitting potential.

## **2.5 Microstructure**

The presence of defects, cracks, dislocations, grains, impurities, particular structures favours the localized corrosion where the attack of the corroding medium is nonuniform over the metal surface. The ion beam treatment is beneficial to interfere with such corrosion mechanisms by formation of solid solution and surface amorphisation. The heterogeneity of both structural and chemical nature will be reduced. It was reported that changes in the two phase microstructure ( $\alpha$  and  $\beta$  microplates) correlate with the improved resistance on N implanted Ti6Al4V to standard etchant solutions [49]. The effect of Ta and Ni implantation on the corrosion behaviour of Ti has been studied by Sugizaki et al. [103]. TEM and TED analysis results identified characteristic microstructures and phases in both cases which may be made, to a certain extent, responsible for the improved corrosion behaviour

observed.  $\beta$ -phase was seen in the Ta implanted layer with the grain size for precipitates of 30 - 150 nm. In Ni implanted layers intermetallic  $Ti_2Ni$  precipitated in a more fine grain size of ca. 8 nm. As both Ta and Ni have low solubility in the  $\alpha$ -phase, their implantation tends to form the  $\beta$ -phase or  $Ti_2Ni$  via the eutectoid reaction. Wolf et al. [138] have shown the dominant role of the phase formation for nitride in determining the corrosion behaviour. For nitrogen implanted Fe they found that a uniform  $\gamma'$ - $Fe_4N$  phase reduces the Fe corrosion by about three orders of magnitude, while an implanted surface without  $\gamma'$ - $Fe_4N$  does not reveal any effect. The formation of the latter was bound to controlled implantation conditions and temperature regime. Similar results were obtained with carbon ion implantation under formation of  $Fe_3C$ . The formation of solid solutions with improved corrosion behaviour has been demonstrated in early works by Ta implantation [139], Ne, Ar, Cu, Pb and Au implantation [96] in Fe, and Hg implantation in Al [140]. Hashimoto [141] has shown that the amorphous state has a higher level of corrosion resistance compared to the crystalline form of the corresponding alloy. The liquid quenching technique is a conventional way to produce an amorphous state, but limited to a narrow composition range. Extremely high quenching rates, as achieved by ion implantation, ion beam mixing or sputter deposition allow materials to be amorphized in a wider composition range. Metals and ionically bonded materials have long range and non-directional interatomic interactions, thus can reorder readily after an implantation perturbation. Implantation and ion beam mixing have been demonstrated to form amorphous Fe-B phases in the sub-surface region of Fe substrate or at the interface [142-145] and such surfaces exhibited improved corrosion behaviour. Implants such as B, P, and large ions have been shown [146] to be efficient in producing amorphisation. Clayton et al. [147] studied the corrosion behaviour in  $H_2SO_4$  and  $H_2SO_4 + NaCl$  of stainless steels amorphized by implantation of B, P or P + B. A reduction in the critical current density for passivation was observed only for P implantation, while the effect of B implantation was to inhibit the pitting attack. Hubler et al. [148] produced amorphisation on steel by using high fluences of  $Ti^+$  ions. The amorphous surface was believed to be stabilized by a Fe-Ti-C layer with carbon, originated from ambient vacuum and incorporated concurrently with the Ti implantation. The corrosion resistance tested in  $H_2SO_4$  and NaCl was improved only weakly. Generally it is difficult to separate various surface corrosion phenomena by measuring the corrosion current. The latter is an integral (practically relevant) parameter averaged over an extended surface region, while the various effects are likely to be efficient in localized micro-regions. The amorphous state experimentally created is not absolutely ideal for excluding such micro-heterogeneities, which can additionally develop during the measurement! This seems to reason the results reported above.

### **3 Thermal Oxidation Resistance**

The effects of ion implantation on thermal oxidation of metals have been extensively studied. The relevant results have been reviewed by Dearnaley [149]. Ba, Sr, Ca, Rb, Cs, and divalent rare-earth elements Yb and Eu were found to be very effective in the inhibition of oxidation of Ti [150,151]. The protection mechanism was related to the blocking of the transport paths (grain boundaries and dislocations) of oxygen or cations by precipitates of a perovskite phase  $\text{MeTiO}_3$ . This effect was found to be valid also for stainless steel implanted with Y and Al [152], nickel implanted with Ce [153], Ni-Cr alloys implanted with Ce [154,155], chromium implanted with La [156]. Another class of implanted ions is prone to develop a coherent films (oxide such as  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{SiO}_2$  or spinel such as  $\text{CuAl}_2\text{O}_4$ ,  $\text{CuCr}_2\text{O}_4$ ) strongly resisting further ion transport. Examples of oxidation resistance along this line are Al implantation into FeCrAlY-alloys [157], and copper and copper alloys [158,159], rare-earth ion implantation into Cr [160,161], Y implantation into stainless steel [162], and NiCr alloys implanted with Y, Hf or Zr [163]. Additives introduced by ion implantation may catalytically participate in producing an oxidation resistance. This mechanism was observed for Cu implanted with Pt, Cr or Al [159], rare-earth ion implantation into Cr [160,161] and cobalt [149] and Pt implantation into CrAl alloys [164]. Many oxides are semiconductors, and ion implantation can modify the conductivity type, thus leading to the formation of p-n junction. If the electron transport is rate-determining factor, the oxidation may be inhibited. This effect was observed for copper implanted with C, Li, W, Bi, Ti, Ni or Eu [165]. There were exceptions regarding Xe and Cs and other implants. The experiments of Ratcliffe and Collins [166] covered 22 chemical implant species and yielded only limited support to this model, suggesting that other inter-related parameters exist. Boron implanted copper and copper oxide ( $\text{Cu}_2\text{O}$ ) are such an example. Ding et al. [167-169] related the improved oxidation resistance to boron filling the negative vacancies in the p-type semiconductor copper oxide, and thus blocking the transport path of  $\text{Cu}^+$  ions. This in turn results in the  $\text{Cu}_2\text{O}$  being oxidized at the surface to a more dense, self-passivating oxide  $\text{CuO}$ .

### **4 Stimulating Surface Bioreactivity**

The surface chemistry has been recognized to be a major factor in controlling the interfacial reactions between the biological medium and the foreign biomaterial. These interactions are predominantly of chemical and biochemical nature including ion exchange, protein adsorption, cell attachment and population, mineralization, all play a part in the healing process and tissue - material bonding [2,10,12,13,41]. Results on using ion implantation to improve surface bioreactivity have been

appeared only very recently. Kelly et al. [170] showed that the growth of anchorage dependent cells to a substrate can be significantly influenced by ion implantation. Röstlund et al. [171] inserted nitrogen ion implanted titanium in the rat abdominal wall and studied its soft tissue response. They observed a predominated collection of macrophages and multinuclear giant cells around the ion implanted surface. The macrophages were large and of active appearance compared to those observed on the unimplanted titanium surface. In vivo experiments in rabbit cortical bone with nitrogen implanted Ti and Ti6Al4V were performed by Johansson et al. [172] to study the hard tissue response. Despite differences in surface characteristics in comparison with unimplanted samples, neither major differences in the degree of bone-implant contact, nor effect on tissue response were found. Ti and Ti alloys have been shown to possess a remarkable biocompatibility behaviour to take up  $\text{Ca}^{2+}$  and  $(\text{PO}_4)^{3-}$  ions from the simulated body fluid and to form calcium phosphate on their surface [173]. Recently, Hanawa et al. [174] have demonstrated that the precipitation of calcium phosphate is substantially increased by Ca implantation into Ti. Surprisingly, they concluded that implanted Ca does not participate in the calcium phosphate formation, but its effect is only catalytical. It was believed that hydrated phosphate ions are initially adsorbed on the surface followed then by an adsorption of calcium ions to the former leading to the formation and precipitation of calcium phosphate. In all, detail of the mechanism is not clear. Walsh et al. [175] considered the aspect of surface charge in controlling cellular interactions at the prosthesis - biomedium interface. For this purpose the morphological response of bone cells grown on silicon surface implanted with Si, Mg, Ti or Cu ions was evaluated and electrokinetic characteristics of the ion implanted surfaces were determined by measuring streaming potential. Osteoblast growth, proliferation and morphology appeared to be influenced by the presence of an implanted ion and the electrokinetic behaviour was shown to depend on ion implantation. This suggests that cells may be responding to the different electrokinetic environment as a result of ion implantation. However, it was not able to correlate surface charge and cell response and the mechanistic detail of the interfacial processes is not known. Surface charges and potentials are considered to be involved in generation, repair and remodelling of bone [176,177]. Functional groups (on polymeric surfaces), most of which are charged, enhance in-vitro osteoblastic colonization [178], and beads, when carrying a negative charge, enhance the formation of bone in vivo [179]. Howlett et al. [180] measured contact angles and the strength of attachment of individual cells to a silicon surface pretreated by ion implantation. There was no evidence of an increased adhesion of human bone derived cells produced by implantation with N, P, Mn or Mg. A correlation was found between wettability and rate of cell attachment to oxygen implanted surface. The Mg implantation into  $\text{Al}_2\text{O}_3$ , a ceramic material commonly used in orthopedic devices, significantly increased the attachment and spreading of cultured human bone cells and markedly affected the morphology of the latter [181]. Divalent cations, such as  $\text{Ca}^{2+}$ , a bone constituent, and  $\text{Mg}^{2+}$ , are known to be active in cell adhesion

mechanisms [182]. The effects of ion implantation into polymers have been reported by Lee et al. [183], Suzuki et al. [184] and Li Dejun et al. [185]. Endothelial cells are not capable of proliferating on polymers such as polyurethane and polystyrene. The adhesion and proliferation of endothelial cells were drastically improved on ion implanted surfaces. But the effect was seen to be independent on the implanted ion species used including  $\text{Na}^+$ ,  $\text{N}^+$ ,  $\text{O}^+$ ,  $\text{Ne}^+$ ,  $\text{Ar}^+$ ,  $\text{Kr}^+$ . It was concluded that the same carbon structure produced by ion implantation is responsible for the observed results [183,184]. Significant changes in wettability, blood adsorption, anticoagulability and anticalcification were reported for polyurethane implanted with  $\text{Si}^+$  [185]. Again, some degree of surface destruction in form of bond breaking was detected by XPS, but an assignment was impossible.

## **5 Matching Tribomechanical Parameters**

Medical devices used in orthopedics and dentistry are force bearing and contain in most cases articulating surfaces, such as in hip or knee prostheses or in bone plates. The choice of bulk material is governed by its fatigue and fracture resistance, but the surface properties are likely to be determined by other criteria, such as wear and friction resistance, in addition to being biocompatible. One strategy to reach adequately all requirements, often very conflicting, is the surface modification without sacrificing important mechanical bulk properties. Surface layers can be deposited by conventional techniques, but the ion beam process offers potential advantages regarding variability in composition, solid solubility, interfacial adherence etc. The tribomechanical properties modified by ion implantation have been reviewed for the most part for industrial applications [49,186,187] and in a limited extent for biomaterials [48,89,91]. Titanium and titanium alloys are being used increasingly in biomedical applications. The major beneficial bulk properties are ductility, tensile and fatigue strength, and bone-matched modulus of elasticity [190]. However, they undergo excessive wear during use in the human body. Nitrogen ion implantation leads to a substantial improvement of wear resistance [48,52,91,191-193] tested in various simulated synovial fluids and to a reduction of friction [64,67]. The corrosive wear of Ti6Al4V implanted with  $\text{N}^+$  was measured by Williams and Buchanan [52], Dearnaley [54], and Hutchings and Oliver [61] to be reduced by up to 4 orders of magnitude. Beside dissolved nitrogen, the implantation results in the formation of fine TiN precipitates [52,56-68]. The particles [59,62,63,66,68] are ~ 10-150 nm in size, depending on the implantation conditions [63,64,67]. The lifetime of wear resistance increased with increasing implanted dose and the saturation in wear resistance as a function of ion dose [194] was related to the limit in the dislocation line density. An optimal substrate temperature was given to be ~ 470-500 °C [63,64]. The interpretation accepted [52,61,187,193] is the conjoint effect of surface hardening and chemistry. The hard TiN precipitates are efficient obstacles to dislocation

movement, a factor encouraging the plastic deformation. The hardened surface provides improved support for a well adhering low friction sub-oxide film  $\text{TiO}$  which was thought to be stabilized by implanted nitrogen [60], thus resulting additionally in speeding the repassivation. Oliver et al. [58,61] discussed a possible quick repassivation by a protective oxy-nitride film  $\text{TiON}$  formed from dissolved nitrogen, in place of  $\text{TiO}_2$ . For Ti and Ti alloys there is no evidence of a retention of wear resistance over worn depths in excess of the ion implanted zone. The normal wear behaviour returns at the break-through depth [58,61] equal to the implanted layer. The wear resistance and microhardness of steels and other materials implanted with nitrogen were shown to remain in a high level even after the implanted nitrogen has been removed completely [188,195-201]. The phenomenon was interpreted [195,196] in terms of an oxidative wear mode and an inward propagation of implantation induced dislocation structures.

As with nitrogen, carbon implantation [59,62,63,65,70,201] improves wear behaviour via  $\text{TiC}$  precipitation [62,70,201] and friction behaviour via a sub-oxide film  $\text{TiO}$  supported by  $\text{TiC}$  containing implanted layer [64,67,70]. A thermal post-treatment at  $400^\circ\text{C}$  resulted in growth and redistribution of  $\text{TiC}$  precipitates [59,70] leading to further enhancement of the implantation effects [70]. The temperature effect (substrate heating or post annealing) has been reported [71,202-204] to be beneficial in increasing the hardness and wear resistance. C and N were observed to be equally efficient in hardening pure Ti, but C being less efficient in increasing the hardness [65] and more effective in increasing the fatigue resistance of the  $\text{Ti6Al4V}$  alloy [59,201]. The effect was related to the  $\beta$  phase in the alloy. Titanium is susceptible to fatigue failure with crack initiation caused by local fretting. The great improvement in fatigue resistance of carbon implantation was thought [59,201] to be related to the compressive stress in the surface and the interaction between the implanted layer and the bulk material. Nucleation of subsurface fatigue cracks can occur as deep as 25-150  $\mu\text{m}$  below the surface [189].

That the wear resistance and friction behaviour relate to certain compounds (nitride, carbide, oxide, and mixed form of them) created by ion implantation was also confirmed by implantation of  $\text{Ti}^+$  [205] and  $\text{Ta}^+$  or  $\text{Nb}^+$  [206,207] into steel alloys. All these elements are reactive toward N, C and O.

Another mechanism producing surface hardening relies on the mechanical energy absorption resulted from changes in microstructures [187]. The cubic-to-tetragonal transformation of martensitic structure can be used once to absorb energy. The increase in work hardenability of cobalt brought about by nitrogen implantation was identified by Dearnaley [208] to be related to stabilizing the cubic austenite or the fcc structure of cobalt.

The strain field produced by asymmetric atom pairs has been revealed to be a further factor in controlling the mechanical surface properties, as it interacts strongly with that of a nearby dislocation [209-211]. An oversized substitutional atom linked to a small interstitial neighbour is such an asymmetric atom pair. Wear reduction for



stainless steel was observed by implantation of Y, an oversized atom, followed by N or C implantation [209-212].

## 6 Ceramics

Ceramics, inorganics, and glasses are widely used in the health care industry. There is a multitude of materials, newly developed [12-15] having finely adjusted biocompatibility, ranging from nearly bioinert (e.g. dense and nonporous alumina) to highly bioactive (e.g. hydroxylapatite). Major limitations on clinical use of ceramics are related to the insufficient or tissue-non matched mechanical properties and aqueous corrosion. There are two aspects of using ion beams for processing bioceramics: a) surface modification to achieve an improved interfacing and b) synthesis and coupling of thin films of ceramics onto metals and alloys, materials with excellent mechanical properties but lacking some degree of biocompatibility. The field is beginning to emerge, and fundamental aspects of ion bombarded ceramic surfaces have been considered mostly with respect to optical properties, tribomechanics, and ionsensing characteristics. The microstructure, including stoichiometry, of ion implanted ceramics (alumina and silicon carbide) has been reviewed [213]. Silica and silica based glasses, phosphate glasses implanted with a wide range of species have been considered in terms of the chemical reactivity and formation of defects.

Aluminosilicate glasses with ion exchange properties equivalent to their conventional counterparts were obtained by implanting alumina with Si and Li [214]. The implantation of  $Al^+$  ions and alkali ions into  $SiO_2$  [215] or oxidized  $Si_3N_4$  [216] led to similar results. A comprehensive study was made of the effect of group III implant ions on the membrane potentials of  $SiO_2$  surface [217]. The ion implantation has been shown to be effective in designing thin films as low as 40 nm having  $K^+$  ion sensitivity [218]. The synthesis of binary compounds of  $Ag_2S$  or silver halides embedded in a thin film matrix of  $SiO_2$  was demonstrated by ion implantation [219] and such surfaces showed specific ion exchange toward silver and halide ions. Thin films of lead phosphate glasses having specific anion adsorption were produced by Nomura and Masui [220] using ion beam sputtering.

The Zr implantation into  $Al_2O_3$  [221] followed by thermal annealing in an oxidized atmosphere resulted in a surface strengthening which was attributed to the small precipitates of  $ZrO_2$ . For  $Al_2O_3$ , chromium implantation [222] increased the surface hardness by 30-40%, and the flexural strength was increased by more than 20 % after nitrogen implantation [223]. The wear resistance of  $ZrO_2$  against  $Al_2O_3$  was shown to be reduced by several orders of magnitude after carbon ion implantation [224]. The combination of a bioceramic material as a coating and a metal or alloy as bulk substrate allows the exploitation of beneficial aspects of the both materials. Ektessabi [225] studied the coating of Ti and stainless steel, two materials commonly used in

orthopedics and dentistry, with thin films of bioinert  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$ , and bioactive hydroxylapatite using IBAD technique. The stoichiometry and the film compactness have been shown to be adjustable by means of the process parameters ion to atom arrival ratio, ion energy, and angle of incidence.

## 7 Advanced Ion Beam Processings

The direct ion implantation suffers from some limitations, such as line-of-sight process, shallow implant depth, and sputter-limited implant concentration. Advanced ion beam processings [226] able to solve these problems, partly or in all, include high current implantation, plasma source ion implantation (PSII) [227-231], ion beam mixing (IBM), ion beam assisted deposition (IBAD), and pulsed ion beam evaporation (PIBE).

High fluence of Hf implanted into Fe [232] resulted in an increase of dislocation density extending up to 100  $\mu\text{m}$  beneath the surface which was directly correlated with a hardness increase. In this process a high implant concentration exceeding the sputter-limited level was achieved due to plasma redeposition of sputter-removed material. Penetrations of N 10 x deeper than the ion range or diffusion depth were observed [233,234] with high fluence implantation into stainless steel at 380-400  $^\circ\text{C}$ , which led to a marked increase in wear life. A metastable austenite phase with up to 20 at.% dissolved N was formed.

Ion beam mixing enhances the coating adhesion by successive events of particle displacement and relocation, or breaking and reforming of chemical bonds between atoms at the interface. Chemical reactions are involved, if the ion species are reactive. Nitrogen implantation through a boron film deposited on Fe [235,236] resulted in the formation of a B/Fe mixed layer and a buried BN phase. Iron boride formation has also been reported [143]. The resultant composite layer was shown to be greatly beneficial in protecting Fe from corrosion in acidic solutions. Many parameters were thought to interplay, including interfacial adherence, chemical inertness and barrier to interdiffusion of BN and of the boron outermost film. Elena et al. [108] compared the effectiveness of  $\text{Kr}^+$  and  $\text{N}^+$  ions in mixing a 100 nm thick multilayer  $\text{Fe}_{80}\text{B}_{20}$  deposited on Fe by alternately sputtering Fe and B. The corrosion resistance after  $\text{N}^+$  ion mixing was greater, but not significantly, compared to  $\text{Kr}^+$  ion mixing, indicating some BN effect. But, in both cases an increase in corrosion was observed compared to unprotected Fe. The effect was believed to be due to Fe present in the film. These results led Elena et al. to produce a coherent thick film of B with embedded BN by repeated B deposition and  $\text{N}^+$  ion bombardment. The corrosion resistance and resistance to pitting attack of the film on Fe were found to be markedly increased. Ion beam mixing has been used to incorporate noble metals into Co-Cr alloys [48]. Mixed platinum was effective in reducing corrosion. Surprisingly, a hydrated calcium phosphate was found on such a surface leading to some speculative surface

processing for biocompatibility. The corrosion resistance has been shown for TiN on Fe by ion beam mixing [237]

In the IBAD process the material deposition occurs simultaneously with ion bombardment. Ion energy, ion / atom arrival ratio, angle of incidence and substrate temperature are major process parameters efficiently controlling surface properties, such as microstructure, stoichiometry, stress, porosity, film thickness and adhesion. Evaporation is the conventional technique for Al films, but the Ar<sup>+</sup> bombardment during the Al deposition on Fe or steels markedly improved the aqueous corrosion resistance, as shown by Wolf et al. [238]. Thickness of up to 10 μm was obtained with adhesion strength exceeding that of evaporated films. The angle of incidence has been shown to affect greatly the film adhesion and densification [138]. The columnar growth or textured grains changed or disappeared, as the angle of incidence varied from normal to oblique. A dense film was generated resulting in an efficient barrier to ion transport. The densification is related to events such as forward recoil, lateral displacement and collapse of open structures, as derived from molecular dynamics modelling by Muller [239]. Pinhole-free Cr layers for corrosion protection are difficult to achieve by galvanic coating. IBAD process allowed corrosion resistant Cr layers on Fe with low stress and low porosity to be produced [238]. Without an intermediate layer an amorphous hard carbon film on steels are obtained by CVD only with difficulty. The deposition under Ar<sup>+</sup> ion bombardment yielded carbon films on steel with excellent adhesion and low hydrogen content which showed corrosion resistance and hardness [238]. The improvement of corrosion resistance and resistance to pitting attack has been reported for Si coating on Al [111-113] and on steel [238] using IBAD technique.

Alloying Al film with a less noble metal able to function as a sacrificial anode provides a more effective corrosion protection of steel than a film of pure Al. Such an alloy is e.g. Al/Mg. Enders et al. [240] have shown that the energy of ion bombardment during film growing is an useful parameter to adjust an optimal corrosion protection. Fine grained and adherent films of Nb-Cr were obtained for corrosion protection of stainless steel by Hsieh et al. [241]. Chemical resistant inorganic compounds, such as oxides and nitrides have been grown to greater thicknesses with improved adhesion, low porosity and excellent corrosion resistance on metals and alloys: Ta<sub>2</sub>O<sub>5</sub> [135], Al<sub>2</sub>O<sub>3</sub> [113], TiN [113,242-246], Cr<sub>2</sub>N [138,235], AlN [113,247,248], BN [235,249,250], Si<sub>3</sub>N<sub>4</sub> [114,135,251]. Combined layers have been shown to exhibit multifunctional characteristics [6,31]. For instance, TiC coating with amorphous hard carbon on top has strong wear resistance and low friction. For Al/AlN the inner Al is effective in inhibiting corrosion, while the outer AlN layer imparts wear resistance. Barth et al. [252] have shown that the stress of the IBAD layers remarkably affects the corrosion behaviour. The corrosion of steel coated with Cr was increasingly inhibited as the tensile stress was reduced by increasing Ar<sup>+</sup>/Cr ratio. For compound layers, the authors demonstrated the tailoring of the stress state by using a multilayer growing. An 1 μm thick Ti/TiN multilayer coating on steel in

an optimized compressive stress state was shown to reduce the corrosion by two orders of magnitude.

## **8 Concluding Remarks**

Surfaces of metals, alloys and ceramics subjected to ion implantation or advanced ion beam processings have experienced large modifications, in some cases providing spectacular effects in improving ion release resistance and tribomechanical properties. The susceptibility to biological response was observed for some surface systems. Many attributes of the ion beams are usefull for biomaterials with respect to both basic research and applicative aspects.

Defined and reproducible surfaces with systematically varying chemical composition are one major step for studying elementary processes of biological medium - material surface interactions. These are achievable, including geometry down to nanometer range, more efficiently than any other conventional procedure. The systematical variation of additive concentration, by the way, is one reliable way to eliminate the contamination effect.

The ion and electronic transport in thin solid films is often the factor that governs the rates of the interaction of the material with the surrounding. The microstructures, type of conductivity, the porosity, and stress state, if definitely and systematically controllable, are useful parameters to modulate this process. Again, ion beam processing is beneficial for this purpose.

The synthesis and coupling of a biocompatible layer onto a metal or alloy using ion implantation or advanced ion beam procedures is an alternative solution to the adherence problem encountered with conventional coatings. The film properties that can deliberately be modified and controlled cover a broad range, as indicated above. Some materials which can serve as model substance may be apatite, bioactive glasses,  $Al_2O_3$ ,  $TiO_2$ ,  $Ta_2O_5$ , and  $TiN$ .

The ion release process and its subsequent involvement with the biological environment or their concurrent occurrence due to the mutual interactions are governed by a number of mechanisms involving a multitude of parameters. Discriminating these various effects and phenomena is a first step to improve the understanding of biocompatibility. Many traditional techniques and procedures for characterizing properties provide an integral result. The corrosion current, corrosion potential, or polarization characteristics are typical examples of such limitations. Time and space resolved, and in situ measurement and preparation techniques, allowing

recording of the earliest stage of events and down to sub- $\mu\text{m}$  geometry, will be helpful in improving the situation. Optical and microscopic techniques, such as anisotropy microellipsometry, scanning force and tunneling microscopy with in situ electrochemical measurement appear to be efficient to advance fundamental knowledges on the molecular level.

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