FAILURES OF STAINLESS STEEL ORTHOPAEDIC DEVICES – CAUSES AND REMEDIES

U. Kamachi Mudali1,*, T.M. Sridhar2, N. Eliaz2 and Baldev Raj1

1Metallurgy and Materials Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India
2Biomaterials, Medical Devices & Corrosion Laboratory, Department of Solid Mechanics, Materials and Systems, Tel-Aviv University, Ramat-Aviv, Tel Aviv 69978, Israel

* Email: Kamachi@igcar.ernet.in

ABSTRACT

Orthopaedic implants are exposed to the biochemical and dynamic environments of the human body; their design is dictated by anatomy and restricted by physiological conditions. In every failure of an orthopaedic implant, the concerned patient is made to experience the trauma of repeated surgeries, besides the severe pain experienced during the process of rejection of the device. The removal of the failed implant will cause great expense and hardship to the patient. Therefore, it is highly desirable to keep the number of failures to a minimum. The determination of the mechanism by which failure of an implant occurred is important, but it is also necessary to explore the event, or sequence of events, that had caused a particular mechanism or mechanisms to be operative. Furthermore, failure analyses can help improving the overall performance of implant devices through revision engineering.

In the framework of this study, a survey of failure investigations of stainless steel implants was undertaken. The use of advanced stainless steels and the application of nitrogen ion implantation and bioceramic hydroxyapatite coatings as potential remedies are evaluated. Failure analyses reveal the occurrence of significant localized corrosion attack viz., pitting and crevice corrosion. These findings support the need for the development of some innovative implant materials exhibiting resistance to localized corrosion attack. Cooperative efforts by the materials and medical/surgical
disciplines may result in even greater improvements in the future with respect to the durability and safety of these implant devices.

1. INTRODUCTION

1.1 Failure analyses of failed orthopaedic implant devices

Metallic orthopaedic implants are often mounted into the skeletal system of the human body as constituents of reconstructive devices (e.g., hip or knee joint replacement) or fracture fixation products (e.g., plates, screws and nails). The design of these implants is dictated by the anatomy and restricted by the physiology of the skeletal structure of the human body /1/. The mechanical and chemical stabilities and biocompatibility of the implant materials in the environment of tissues and body fluids are of fundamental importance for the successful treatment of bone fractures and bone replacements. An orthopaedic implant is considered to have failed if it has to be prematurely removed from the body. Failures of implants are usually classified as either mechanical, electrochemical or biological. Mechanical failures include permanent deformation, overload fracture, fatigue fracture, and wear. Electrochemical failures are related to different forms of corrosion. Biological failures are due to infection, inflammation, or other adverse reactions in the host induced by the presence of the implant. Failures may also result from synergistic combinations of these processes.

In spite of the recent innovative metallurgical and technological advances, and the remarkable progress in the design of medical devices, failures of implants do occur. Although failures of implants are often attributed to fatigue, corrosion, wear and/or other failure mechanisms, the underlying causes of failures are seldom determined. These causes may be associated, for example, with biomechanical factors rather than with problems in the basic design of device and/or metallurgy of the implant material. In this work, the failure of stainless steel implants is analyzed. The remedies to overcome such failures are highlighted, focusing on alloy as well as surface modification, for example through nitrogen ion implantation or bioceramic coatings. The effects of these modifications are found to be satisfactory with respect to prevention of corrosion-related failures.
1.2 Why failures are not tolerable?

In situ degradation of metallic implants may decrease the structural integrity of the implant. In addition, metal ions, which are released as degradation products, are transported by body fluids to remote tissues where they may elicit an adverse biological reaction (such as cytotoxicity, allergy, or even cancer). Many authors have reported increased concentrations of local and systemic trace metal in association with metal implants. Moreover, accelerated corrosion and tissue response that can be related directly to identifiable corrosion products have been demonstrated in the tissue surrounding multiple-part devices [2].

Histological sections of the tissue surrounding stainless steel internal fixation devices generally show encapsulation by a fibrous membrane with little or no inflammation over most of the device. However, at the screw-plate junctions, the membrane often contains macrophages, foreign-body giant cells, and a variable number of lymphocytes in association with two types of corrosion products: iron-containing hemosiderin-like granules, and microplates, which consist of relatively larger particles of chromium compound. Solid products of corrosion also have been reported in association with accelerated corrosion of stainless steel femoral stems and spinal instrumentation [2]. Jones et al. [3] observed substantially elevated serum chromium levels in patients with modular femoral nails made of 316L stainless steel. Radiographic findings of osteolysis, periosteal reaction and cortical thickening were related to particulate debris formed by fretting corrosion.

Hallab et al. have reviewed several concepts on metal sensitivity in patients with orthopaedic implants [4]. Merritt and Brown [5] also reported the ability of metallic implants to stimulate metal sensitivity reactions upon degradation. It is apparent that the presence of metal ions in sensitive animals or humans may elicit an inflammatory response and have an adverse effect on the performance of the implant with pain, swelling and tissue necrosis at the site. It has been found that metal ions, which are released from implants in vivo, mostly bind to albumin; their ability to bind to red and white cells varies, hexavalent chromium cations binding most strongly. The binding of certain metal ions to tissues and proteins may be altered by slight increase in pH around the tissue during inflammatory response or infection. Studies have indicated that metallic ions released during corrosion of stainless steels accumulate in the liver and kidneys and are responsible for morphological
changes in these organs /6/. Hence, it is necessary to keep the corrosion and number of failures to a minimum by developing materials with improved properties for the specific body environment.

1.3 Survey of failures

A survey of failures of stainless steel orthopaedic implants, retrieved from various patients in local hospitals in Chennai (Madras), India, was conducted over a period of four years (1988-1991). During this period, 700 cases of premature removal were recorded. Only 50 interesting cases, for which details regarding the clinical history and causes of removal were available from the hospital sources, were chosen for the study /7/. These 50 failed implants were sorted based on the reported causes of removal, type of device, anatomical location, implant lifetime, and number of components in the device, as discussed in the following sections.

1.3.1 Sorting of failed implants according to the reported cause of removal

The sorting of all failures according to the reported cause of removal is given in Table 1. The incidence of fracture was about 42%, while that of corrosion was about 24% of total implants. However, corrosion damage (pitting, crevice and fretting) was also observed in implants removed because of fracture, adverse tissue reaction, wear and cracking without fracture. These observations emphasize the significant role of corrosion in stainless steel implants failure.

Table 1
Classification of the fifty failed implants based on the reported cause of removal.

<table>
<thead>
<tr>
<th>Reported cases</th>
<th>Number of Implants</th>
<th>% Incidence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fractured implants</td>
<td>21</td>
<td>42</td>
</tr>
<tr>
<td>Corroded implants</td>
<td>12</td>
<td>24</td>
</tr>
<tr>
<td>Adverse tissue response</td>
<td>7</td>
<td>14</td>
</tr>
<tr>
<td>Cracks without fracture</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Wear</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>Bending without fracture</td>
<td>3</td>
<td>6</td>
</tr>
</tbody>
</table>
1.3.2 Classification of failed implants based on anatomical location

Classification of failures based on their anatomical location is given in Table 2. About 74% of the implants failed at the femoral head, neck, shaft and condyle areas. In addition, 8% of all cases were removed from knee, 4% from the tibia, 2% from the humeral area, and 12% from the radius and ulna. As mentioned earlier, complicated biomechanical forces are imposed on the femoral area compared to other anatomical sites; these forces would have been responsible for the majority of implant failures. The observed results complement the results of Taussing, who reported about 76% of the implant failures in the femoral area; 8% in the knee, 2% at the tibial area, and over 12% from the radius and ulna regions. According to him, the remaining 2% of the failures were encountered in the humeral area, where the imposed biomechanical force is far less.

Table 2

Classification of the fifty failed implants based on their anatomical location.

<table>
<thead>
<tr>
<th>Anatomical location</th>
<th>Number of implants</th>
<th>% incidence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Femoral head and neck</td>
<td>21</td>
<td>42</td>
</tr>
<tr>
<td>Femoral shaft and condyle</td>
<td>16</td>
<td>32</td>
</tr>
<tr>
<td>Radius and ulna</td>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>Knee</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Tibia</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Humeral</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

1.3.3 Classification of failed implants based on their lifetime

The occurrence of various types of failures with respect to implant lifetime was evaluated and classified into three groups (Table 3). Among the 9 cases under group 1 (hip and knee implants), three were fractured within an implantation period of 6 to 30 months. Moreover, three implants failed within a period of 31 to 50 months due to high wear levels of the acetabular cup. The premature removal of implants under group 1 could often be attributed to the inept mobility of the patients. In certain cases, the patients were unaware of the resulting high load imposed on the bone at the site of implantation, which lead to an early failure of the implant. Hence, it is important that
<table>
<thead>
<tr>
<th>Type</th>
<th>Implantation period (months)</th>
<th>Group I</th>
<th>Group II</th>
<th>Group III</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Hip and knee implants</td>
<td>Intertrochanteric nail/plate</td>
<td>Intramedullary nails, rust nails, fixation pins and bone screws</td>
</tr>
<tr>
<td></td>
<td>2-10</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>11-15</td>
<td>2</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>21-25</td>
<td>1</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>26-30</td>
<td></td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>31-35</td>
<td></td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>36-40</td>
<td></td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>46-50</td>
<td></td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>
surgeons give proper counseling to their patients to avoid recurrence of such premature failures.

Among the 23 cases under group II (intertrochanteric nail/plate combination and bone plates), three were removed within an implantation period of 1 to 5 months. In addition, eleven implants were removed due to corrosion and six were removed due to fracture within an implantation period 6 to 25 months. Bending of implant not accompanied by fracture was observed in two cases. Once again, the predominance of corrosion and mechanical fracture as causes of implant failure is evident.

Failure analyses of bone plate fractures indicated that 85% of them originated from the countersunk hole closest to the center of the plate, while the remaining fractures originated from the second hole relative to the center of the plate. Generally, the bone plates are surgically fixed so that their center area overlaps with bone fracture. Hence, the highest stresses are expected to operate around the screw hole closest to the center of the plate, and then around the second screw hole. This observation is similar to that of Taussing /8/, who reported that 95% of the fractures in bone plates occur at the first screw hole, the remaining 5% occurring at the second screw hole relative to the center of the bone plate.

Finally, one of the 18 implants under group III (intramedullary nails, rust nails, fixation pins and bone screws) was removed within 5 months of implantation due to an adverse tissue response. Three additional failures due to an adverse tissue response were observed within 6 to 15 months of implantation. Ten implants were observed to be fractured within 6 to 25 months of implantation. Corrosion attack was observed in only one case, while bending without fracture was noticed in one case.

1.3.4 Corrosion encountered in single- and multi-component devices

The data becomes more informative if the results are interpreted in terms of frequency of corrosion attack in the single- and multi-component devices separately, as shown in Table 4. Here, a multi-component device is defined as one having two or more components, for example a plate in conjunction with screws. On this device, corrosion generally occurs where the metal surfaces of the two components are in intimate contact with each other. In the case of bone plates, the plates are fixed on the bones by using screws, which create a crevice between the screw head and the plate hole. This deep crevice acts as a preferred site for corrosion attack. Moreover, in the case of bone plates, the frequency of crevice attack is fairly high. Apparently, when conditions are
Table 4
Relative incidence of crevice corrosion in single- and multi-component failed devices.

<table>
<thead>
<tr>
<th></th>
<th>Single-component devices</th>
<th>Multi-component devices</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total number of devices</td>
<td>16</td>
<td>34</td>
</tr>
<tr>
<td>Number of corroded devices</td>
<td>1</td>
<td>11</td>
</tr>
</tbody>
</table>

Favourable, corrosion in the crevice nucleates soon after implantation. Corrosion could be detected in several implants that had been in human body for two months; the corrosion became more pronounced as the implantation time increased. Among the 12 severely corroded implants analyzed in this study, eleven (about 91%) were multi-component devices (namely, bone plates and screws). This finding supports an earlier observation of Scales et al. /9/, who reported significant corrosion incidence at interfacial sites as compared to the non-interfacial fixation components. Colangelo and Greene /10/ also reported a marked increase in the incidence of crevice corrosion in multi-component devices made up of type 316 stainless steels as compared to single-component devices.

The data from the present study can be further analyzed, as shown in Table 5. In this table, the incidence of crevice corrosion is expressed in terms of the total number of metal-metal interfaces, with multiple holes and screws; the countersunk holes on the corresponding plate were individually examined.

Table 5
Incidence of crevice corrosion in failed devices.

<table>
<thead>
<tr>
<th></th>
<th>Number of hole/screw interfaces</th>
<th>Number of corroded holes</th>
<th>Number of corroded screws</th>
<th>Number of other interfaces</th>
<th>Number of other corroded surfaces</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multi-component devices</td>
<td>103</td>
<td>42</td>
<td>36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single-component devices</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>1</td>
</tr>
</tbody>
</table>
for evidence of corrosion. Thus, out of 103 hole-screw interfaces existing in 19 plates, approximately 34% of the holes and 28% of the screws were found to be corroded. In other interfaces, such as in intertrochanteric nail/plate combinations and total knee replacement, corrosion was observed only in one out of five cases. Altogether, crevice corrosion was observed on more than 37 interfaces (34%) in the failed devices. This percentage of incidence is considerably higher than the average incidence (13.5%) of corrosion reported by Scales et al. /9/, but lower than the average incidence (41%) reported by Colangelo and Greene /10/.

1.4 Origin and mode of failure in failed stainless steel orthopaedic devices

The determination of the origin and mode of failure in orthopedic devices provides may be used as a tool for improving the overall performance of these devices. Among the 50 failed cases presented in the previous section, 10 cases with different origin and mode of failure were selected arbitrarily for detailed failure analyses. These analyses were performed as per standard recommended procedures /11/. The sequence of steps employed to investigate the origin and mode of failure is given as a flow chart in Fig. 1. The selected ten case studies are summarized in Tables 6.1 and 6.2. The chemical composition of the implant materials is given in Table 7 along with the typical ASTM standard values for comparison. From this table it is evident that the chemical composition of the implant materials examined in the present study is well within the limits recommended by ASTM /11/.

1.5 Corroboration of failure mechanisms

Detailed analysis of the failed implants, case histories and radiographs of the 10 different cases studied indicated the following possible causes of failure:

a) Inept mobility and unawareness of the patient on the load-bearing capacity of an implant.
b) Improper fitting of the implants by the surgeons.
c) Biomechanical forces.
d) Corrosion attack due to hostile body environment.
e) Fabrication problems – deviation of material properties (namely, chemical composition, inclusion content and grain size) from the requirements of medical standard specifications, improper heat treatments, imprint marks on the implants, etc.

![Flowchart Diagram]

**Fig. 1:** Correlation diagram showing the conjoint action of two failure mechanisms in several of the ten selected failed implants.
### Table 6.1
Survey of failed orthopaedic implants – case studies 1-5.

<table>
<thead>
<tr>
<th>Case No.: sex, age and implantation site</th>
<th>Type of implant device</th>
<th>Mechanism and cause of failure</th>
<th>Major findings</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: Male, 21 years, radius of the right hand</td>
<td>Broad hole compression plate</td>
<td>Biomechanical force induced fatigue failure</td>
<td>Fractured area of the radius and ulna (bones), gap between fractured faces of bone at the site of bone fracture. Pitting potential of failed implant ($E_a = +370 mV$) is slightly higher that of ASTM recommended type 316L SS ($E_a = +365 mV$).</td>
<td>No evidence of corrosion in the vicinity of fractured site. Failure is likely not due to material fabrication problem.</td>
</tr>
<tr>
<td>2: Male, 34 years, right femur</td>
<td>6-holes tubular compression bone plate</td>
<td>Fatigue failure of the compression plate due to bad fixation</td>
<td>Fracture of the bone plate at fourth and fifth screw holes; fracture site is visible. Pitting potential of failed implant: $E_a = +385 mV$.</td>
<td>Beach marks originated from asymmetric bending and rotational forces. Implant failed through fatigue mechanism.</td>
</tr>
<tr>
<td>3: Male, 29 years, right femur</td>
<td>Intertrochanteric nail/plate combination</td>
<td>Fatigue failure due to improper fixation</td>
<td>Device broken at the fifth countersunk hole (out of nine) from the plate end. Screw in sixth countersunk is missing. Visibly broken. Pitting potential of failed implant: $E_a = +354 mV$.</td>
<td>Classified as brittle fracture. One screw probably not placed originally as bony fracture exactly coincides with the sixth screw hole. Implant failed through fatigue mechanism.</td>
</tr>
<tr>
<td>4: Female, 62 years, Left femur</td>
<td>Internally fixed rush nail</td>
<td>Fatigue failure due to cyclic overload</td>
<td>Nail fracture coincides with location of the fracture of bone. Pitting potential of failed implant: $E_a = +360 mV$.</td>
<td>Stress at site of bone fracture higher than remainder area. Implant failed through fatigue mechanism. Failed implant not prone to pitting attack.</td>
</tr>
<tr>
<td>5: Female, 26 years, right knee</td>
<td>Total knee prosthesis</td>
<td>Failure due to improper welding</td>
<td>Lower stem of prosthesis bent, crack noticed at the weld joint. Pitting potential of failed implant: $E_a = +345 mV$. Failure could be avoided by using careful welding procedures, dissolving δ-ferrite after welding by high-temperature heat treatment, but this leads to increase in grain size. Best means is to design a single-piece forging rather than a welded assembly.</td>
<td>Improper welding lead to large holes, porosity and δ-ferrite. In the absence of any inspection, this reduced the fatigue lifetime of the prosthesis. Failed implant not prone to pitting attack.</td>
</tr>
<tr>
<td>Case No.: sex, age and implantation site</td>
<td>Type of implant device</td>
<td>Mechanism and cause of failure</td>
<td>Major findings</td>
<td>Remarks</td>
</tr>
<tr>
<td>-----------------------------------------</td>
<td>------------------------</td>
<td>--------------------------------</td>
<td>----------------</td>
<td>---------</td>
</tr>
<tr>
<td>6: Male, 27 years, Right femur</td>
<td>Compression bone plate and screws fixation device</td>
<td>Fatigue failure originating from a pit</td>
<td>Fracture occurred at the fifth countersunk hole of implant, which coincided with the fracture of bone of the right femur of patient. Pitting potential of failed implant: $E_a +265$ mV.</td>
<td>Compression between screw head and screw hole might have aggravated the fracture. Pit could be site of origin of fracture. Implant failed through fatigue mechanism. Failed implant is highly susceptible to pitting. Low Mo content and high inclusion content could have reduced pitting corrosion resistance.</td>
</tr>
<tr>
<td>7: Male, 27 years, Right femur</td>
<td>Kuntscher's clover leaf intramedullary nail</td>
<td>Pit-induced stress corrosion cracking</td>
<td>Hairline crack at site of bone fracture. Pitting potential of failed implant: $E_a +280$ mV.</td>
<td>Low Mo content could have reduced pitting corrosion resistance. Failed implant highly susceptible to pitting.</td>
</tr>
<tr>
<td>8: Female, 71 years, right femoral head and neck</td>
<td>Thompson femoral head prosthesis</td>
<td>Failure due to wear</td>
<td>Severe wear, visible pits and mechanical damage of femoral stem, along with severe corrosion attack with large pits. Pitting potential of failed implant: $E_a +210$ mV.</td>
<td>Low Mo, Cr and Ni and high C contents increased susceptibility to pitting attack. Failed implant highly susceptible to severe wear, pitting and mechanical damage.</td>
</tr>
<tr>
<td>9: Male, 53 years, right neck of the femur</td>
<td>Austin Moore femoral head prosthesis</td>
<td>Fatigue cracks emanating from pits</td>
<td>Loosening of the implant, bone cement broken at the proximal head of prosthesis, and hairline cracks observed. Edges severely pitted, typical cracks originated from pits. Letters of imprinting names and numbers by manufacturers; the microcracks lead to fracture of the implant Pitting potential of failed implant: $E_a +240$ mV.</td>
<td>High inclusion content, large grain size and low Mo content increased susceptibility to pitting attack.</td>
</tr>
<tr>
<td>10: Female, 70 years, ulna in right hand</td>
<td>Sherman bone plate</td>
<td>Corrosion fatigue failure originating from pits and crevices</td>
<td>Fracture occurred at the third countersink hole of plate and coincided with the fractured bone. Fracture and pits were visible. Pitting potential of failed implant: $E_a +335$ mV.</td>
<td>Dissimilar composition of screws and plates lead to galvanic corrosion, resulting in accelerated corrosion. Crevice corrosion at countersink. Pitting attack due to low Mo content.</td>
</tr>
</tbody>
</table>
Table 7
The chemical composition and pitting corrosion potential of selected failed implants.

<table>
<thead>
<tr>
<th>Implant name</th>
<th>Chemical composition %</th>
<th>Pitting Potential (mV vs. SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compression bone plate</td>
<td>19.2 Cr, 12.2 Ni, 2.1 Mo, 2.0 Mn, 0.016 P, 0.251 Si, 0.002 S, 0.031 C, 0.005 Fe</td>
<td>Balance +370</td>
</tr>
<tr>
<td>6-holes tubular compression bone plate</td>
<td>21.3 Cr, 18.0 Ni, 2.5 Mo, 2.1 Mn, 0.015 P, 0.31 Si, 0.092 S, 0.028 C, 0.005 Fe</td>
<td>Balance +385</td>
</tr>
<tr>
<td>Intertrochanteric nail/plate combination</td>
<td>18.2 Cr, 11.9 Ni, 2.1 Mo, 2.3 Mn, 0.093 P, 0.35 Si, 0.003 S, 0.032 C, 0.005 Fe</td>
<td>Balance +354</td>
</tr>
<tr>
<td>Rush Naii</td>
<td>19.5 Cr, 12.2 Ni, 2.3 Mo, 2.1 Mn, 0.016 P, 0.42 Si, 0.005 S, 0.03 C, 0.005 Fe</td>
<td>Balance +360</td>
</tr>
<tr>
<td>Total knee prosthesis</td>
<td>19.2 Cr, 12.5 Ni, 2.1 Mo, 2.0 Mn, 0.017 P, 0.5 Si, 0.02 S, 0.071 C, 0.005 Fe</td>
<td>Balance +345</td>
</tr>
<tr>
<td>Narrow compression bone plate</td>
<td>22.6 Cr, 17.0 Ni, 0.7 Mo, 2.2 Mn, 0.01 P, 0.61 Si, 0.04 S, 0.023 C, 0.005 Fe</td>
<td>Balance +265</td>
</tr>
<tr>
<td>Kuntscher's clover leaf intramedullary nail</td>
<td>18.1 Cr, 10.2 Ni, 1.5 Mo, 2.1 Mn, 0.01 P, 0.52 Si, 0.06 S, 0.03 C, 0.005 Fe</td>
<td>Balance +280</td>
</tr>
<tr>
<td>Thompson femoral head prosthesis</td>
<td>12.2 Cr, 8.5 Ni, 1.2 Mo, 2.3 Mn, 0.02 P, 0.71 Si, 0.05 S, 0.07 C, 0.005 Fe</td>
<td>Balance +210</td>
</tr>
<tr>
<td>Austin Moore femoral head prosthesis</td>
<td>18.1 Cr, 12.0 Ni, 1.2 Mo, 2.1 Mn, 0.05 P, 0.41 Si, 0.05 S, 0.05 C, 0.005 Fe</td>
<td>Balance +240</td>
</tr>
<tr>
<td>Sherman bone plate</td>
<td>19.1 Cr, 11.9 Ni, 2.1 Mo, 2.0 Mn, 0.07 P, 0.51 Si, 0.07 S, 0.021 C, 0.005 Fe</td>
<td>Balance +335</td>
</tr>
<tr>
<td>ASTM 138 - 00 and ASTM F 139 - 00 standard specifications of wrought 316L stainless steel for surgical implants</td>
<td>17.00 Cr to 13.00 Ni, 2.25 Mo to max Mn, 0.025 P to max Si, 0.75 max S, 0.01 max C, 0.03 max Fe</td>
<td>Balance -</td>
</tr>
</tbody>
</table>
A thorough study of the ten selected cases showed that in certain cases only one mechanism of failure was dominant, while in other cases a combination of two or three failure mechanisms led to failure. Hence, a prudent investigation is necessary to determine the mode of failure. The following section is a resumé of the selected case studies interpreted in terms of single-mode failure and conjoint action of two (or more) mechanisms.

1.5.1 Fatigue failure mechanism

Fatigue-related failures were encountered in three cases, namely in a broad hole compression bone plate (case no. 1, Fig. 2), a six-hole tubular compression bone plate (case no. 2, Fig. 3), and an intertrochanteric nail/plate combination (case no.3, Fig. 4).

Typical fatigue failures develop due to cyclic loads that are imposed on the implant and follow three stages – initiation, propagation and overload /12-14/. In the first stage, the crack is initiated at the surface of the implant and grows about one or two grains into the bulk. Local stresses that fall in the

Fig. 2: Radiograph showing an anterior-posterior view of a broad-hole compression bone plate (c) implanted in the radius (R) of the right hand of a 21-years old male patient. Note the gap between the fractured ends of the radius (unlabelled arrow).
Fig. 3: Photograph of the failed 6-hole tubular compression bone plate. Note the fracture of the fifth countersunk hole of the bone plate.

Fig. 4: Stereomicrograph of the fractured surface of the failed intertrochanteric nail/plate implant with characteristic beach marks. The origin of fracture is marked by an unlabelled arrow.
elastic deformation range are sufficient to initiate fatigue cracks. In the second stage, typical fatigue striation marks appear on the broken plates, and the entire fracture surface is related to crack propagation. In the final stage of fatigue cracking, an overload rupture leads to the final fracture.

1.5.2 Conjoint action of two or three failure modes

Among the ten cases described herein, six were related to conjoint action of two failure mechanisms. The combination of fatigue and intergranular corrosion attack was observed in a total knee prosthesis (case no. 5, Fig. 5). In this case, a thick section was welded to a thin section. Hence, the force imposed on the implant by the body was not completely balanced and evenly distributed /15/. The combination of fatigue and overload mechanisms was encountered in the internally fixed rush nail implanted in the femoral area (case no. 4, Fig. 6). Fractography showed that crack propagation proceeded from both sides of the nail; the presence of fatigue striations indicated the involvement of fatigue mechanism /16/.

The combined action of fatigue and pitting corrosion was observed in the compression bone plate and screws fixation device (case no. 6, Fig. 7). The site of bone fracture coincided with that of the implant. The failure of the

---

**Fig. 5:** Photograph of a failed total knee prosthesis. Note that the lower stem of is bent (unlabelled arrow).
Fig. 6: Photograph of a fractured Rush nail. The unlabelled arrow indicates the fractured site of the implant.

Fig. 7: Photomicrograph of a failed compression bone plate and screws fixation device. Note the fracture at the fifth countersunk hole and the scratches on the surface of the bone plate.
compression bone plate resulted from fatigue crack propagation from a corrosion pit /17/. Pit-induced stress corrosion crackling was observed in a severely pitted intramedullary nail (case no. 7, Fig. 8). In both case 5 and case 6, a corrosion pit, which could act as a stress raiser for crack propagation, is likely to be the origin site of fracture. A number of environmental and metallurgical factors may be responsible for pit formation and growth /18-20/. The presence of oxygen, chloride ions and ionic salts in the body environment is reported /18-21/ to act as a pitting agent for stainless steels. Cases 6 and 7 show some similarity in the low molybdenum content. This element, a ferrite stabilizer, is added to austenitic stainless steels mainly to enhance their pitting and crevice corrosion resistance /22/. Several authors /23-25/ have noted the effect of low molybdenum content on the failure of stainless steel implants.

In case 8 (Fig. 9), the Thompson femoral head prosthesis failed due to severe wear encountered at the femoral head. There have already been numerous reports on wear-induced failure of implants, tissue response to wear debris and effect of combining dissimilar metals in total hip replacements (see, for example, Refs. /8, 26-28/). In Case 9 (Fig. 10), the

Fig. 8: Scanning electron micrograph of the crack emanating from the edges of the edge of an intramedullary nail. It may be noted that the crack is associated with a pit.
Fig. 9: Photograph of a failed Thompson femoral head prosthesis.

Fig. 10: Photograph shows the failed Austin Moore femoral head prosthesis.
Austin Moore femoral head prosthesis failed due to fatigue cracks emanating from pits at the head /29/.

Among the ten cases studied, only the Sherman bone plate (case no. 10, Fig. 11) was found to have failed due to the combination of the three failure mechanisms, namely pitting corrosion, crevice corrosion and corrosion fatigue /30/. Fractography revealed the presence of beach marks with dull appearance, possibly indicating the involvement of corrosion fatigue. Moreover, severe crevice corrosion was also observed at the fractured region of the bone plate. The beach marks radiated from a pit in a crevice on the inner wall of the screw hole. This pit could have been origin site of fracture. A similar type of fatigue failure propagating from a pit was encountered in cases 6, 7 and 9. Crack propagation was likely aggravated by the biomechanical forces exerted on the implant.

Fig. 11: A stereo-micrograph of a failed Sherman bone plate showing a crevice corrosion attack at the countersunk hole of the implant.
1.6 Alloy modification of stainless steels: in vitro corrosion behavior

One of the methods to enhance the corrosion resistance of stainless steels is by alloy modification. Alloy modification of stainless steels has been carried out by the authors through addition of titanium and nitrogen as alloying elements as well as evaluation of duplex stainless steels. The corrosion behavior of these alloys was characterized by electrochemical and surface characterization techniques.

Several modified stainless steels, viz. type 316L SS with 680 ppm of nitrogen, 316L SS with 1600 ppm of nitrogen, 317L SS with 880 ppm of nitrogen, 317L SS with 1410 ppm of nitrogen, duplex (SAF 2205) and the super-ferritic (Sea-cure) stainless steels, were studied. The chemical composition of these steels was determined; results are summarized in Table 8 in comparison to that of a reference 316L stainless steel. In vitro corrosion studies were carried out by means of electrochemical methods to evaluate their pitting and crevice corrosion resistance, as well as their susceptibility to accelerated leaching in Hanks simulated physiological solution (Table 9).

1.6.1 Potentiodynamic cyclic polarization studies

The breakdown (or critical pitting) potential, $E_{b}$, is considered herein as a measure of the pitting corrosion resistance of materials. This is the least noble potential at which pitting or crevice corrosion or both will initiate and propagate; an increase in the resistance to pitting corrosion is associated with an increase in $E_{b}$. All potentials were measured using a saturated calomel electrode (SCE) reference electrode and a platinized platinum counter electrode. Detailed experimental details are provided elsewhere /31, 32/. The breakdown potentials of nitrogen bearing stainless steels, 316 titanium-modified stainless steel, SAF 2205 duplex steel and super-ferritic stainless steel were determined from cyclic polarization curves. Major electrochemical parameter values are summarized in Table 10 in comparison with a commercial, surgical grade, type 316L stainless steel (which contains 230 ppm nitrogen).

The mean value of the breakdown potential, $E_{b}$, for type 316L stainless steel was measured as +365 mV. The presence of 680 ppm nitrogen increased the value to +620 mV, whereas the presence of 1600 ppm nitrogen increased the value further to +1170 mV. A similar influence on the $E_{b}$ value was found in the case of type 317L stainless steel containing 880 and 1410 ppm of
<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>Mo</th>
<th>Co</th>
<th>Al</th>
<th>P</th>
<th>Si</th>
<th>S</th>
<th>C</th>
<th>N</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L with 680 ppm of N</td>
<td>17.2</td>
<td>12.7</td>
<td>12.2</td>
<td>2.4</td>
<td>2.05</td>
<td>-</td>
<td>0.017</td>
<td>0.003</td>
<td>0.023</td>
<td>0.021</td>
<td></td>
<td></td>
</tr>
<tr>
<td>316L with 1600 ppm of N</td>
<td>17.9</td>
<td>12.2</td>
<td>12.2</td>
<td>2.45</td>
<td>2.11</td>
<td>-</td>
<td>0.025</td>
<td>0.002</td>
<td>0.023</td>
<td>0.025</td>
<td></td>
<td></td>
</tr>
<tr>
<td>317L with 880 ppm of N</td>
<td>17.4</td>
<td>13.2</td>
<td>13.3</td>
<td>2.58</td>
<td>1.91</td>
<td>-</td>
<td>0.021</td>
<td>0.003</td>
<td>0.068</td>
<td>0.025</td>
<td></td>
<td></td>
</tr>
<tr>
<td>317L with 1410 ppm of N</td>
<td>18.22</td>
<td>13.3</td>
<td>13.3</td>
<td>3.04</td>
<td>2.21</td>
<td>-</td>
<td>0.025</td>
<td>0.002</td>
<td>0.088</td>
<td>0.022</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Duplex</td>
<td>17.6</td>
<td>12.5</td>
<td>14.18</td>
<td>2.22</td>
<td>2.2</td>
<td>0.085</td>
<td>-</td>
<td>0.012</td>
<td>0.001</td>
<td>0.141</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td>Super-ferritic</td>
<td>21.18</td>
<td>5.2</td>
<td>14.18</td>
<td>3.1</td>
<td>3.2</td>
<td>-</td>
<td>0.05</td>
<td>0.013</td>
<td>0.035</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Chemical composition of the modified stainless steels evaluated in this work.
nitrogen (vide Table 10). Thus, it is evident that austenitic stainless steels with higher nitrogen content exhibit increased $E_h$ values, which indicates an improved pitting corrosion resistance under simulated body fluid conditions /33/.

The super-ferritic stainless steel exhibited passivity up to +1120 mV. Beyond this potential, transpassive dissolution took place without exhibiting any pitting attack on the specimen. The mean $E_h$ value was +1189 mV for SAF 2205 duplex steel. Thus, the breakdown potentials of both the super-ferritic and duplex stainless steels were nobler than the currently used type 316L stainless steel. The titanium-modified stainless steel, on the other hand, showed a breakdown potential of +423 mV, which is only marginally higher that that of the reference surgical 316L stainless steel.

Previous reports revealed that the presence of passivating elements in stainless steels increased the pitting corrosion resistance /34-37/. The surgical grade 316L stainless steel contained only 230 ppm nitrogen and 2.4 wt.% molybdenum. Both the nitrogen and molybdenum contents were higher in the modified stainless steels (see Table 8). Wu Yang et al. /38/ reported that the presence of molybdenum in stainless steels inhibits the corrosion process, which apparently increases the difficulty in breaking down the passive film.
Table 10

Electrochemical parameters derived from cyclic polarization curves. $E_a$ is the critical pitting potential, $E_c$ is the critical crevice potential, $E_{corr}$ is the corrosion potential, $E_p$ is the protection potential, and $\Delta E$ is the magnitude of the overall potential range for safe operation.

<table>
<thead>
<tr>
<th>Modified stainless steel materials</th>
<th>$E_{corr}$ (mV)</th>
<th>$E_a$ (mV)</th>
<th>$E_p$ (mV)</th>
<th>$E_c$ (mV)</th>
<th>$\Delta E$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L with 680 ppm of N</td>
<td>-108</td>
<td>-168</td>
<td>24</td>
<td>365</td>
<td>132</td>
</tr>
<tr>
<td>316L with 1600 ppm of N</td>
<td>-159</td>
<td>-155</td>
<td>261</td>
<td>1170</td>
<td>296</td>
</tr>
<tr>
<td>317L with 880 ppm of N</td>
<td>-145</td>
<td>-112</td>
<td>52</td>
<td>1152</td>
<td>64</td>
</tr>
<tr>
<td>317L with 1410 ppm of N</td>
<td>-120</td>
<td>-1189</td>
<td>950</td>
<td>1192</td>
<td>-772</td>
</tr>
<tr>
<td>316 Ti</td>
<td>-200</td>
<td>-1070</td>
<td>-1070</td>
<td>-1070</td>
<td>-1070</td>
</tr>
<tr>
<td>Duplex</td>
<td>-200</td>
<td>-1070</td>
<td>-1070</td>
<td>-1070</td>
<td>-1070</td>
</tr>
<tr>
<td>Super-ferritic</td>
<td>-200</td>
<td>-1070</td>
<td>-1070</td>
<td>-1070</td>
<td>-1070</td>
</tr>
</tbody>
</table>
It has also been reported that the addition of small amounts of nitrogen to welded as well as wrought stainless steels improves their pitting corrosion resistance, sensitization resistance, and mechanical properties /39-42/. A synergistic influence of nitrogen and molybdenum on the pitting corrosion resistance was reported by Truman et al. /43/ and Clayton /44/. Newman et al. /45/ have noticed an enrichment of nitrogen and molybdenum at the passive film/metal interface and related to it the inhibition of further dissolution of the substrate, which is followed by the destruction of the passive film. Kamachi Mudali et al. /46-49/ reported that the addition of nitrogen improves the pitting corrosion resistance of austenitic stainless steels and their weldments; a nitrogen equivalent of 530 ppm was reported per 1 wt% molybdenum in austenitic weld metals. Furthermore, these authors proposed a mechanism by which nitrogen may dissolve at the pit site, form stable nitrate and nitrite films by repassivation, and enhance the pitting resistance by inhibiting pit growth /46, 48/. The immunity against pitting attack of super austenitic stainless steels in 0.5% NaCl solution was also reported by Kamachi Mudali et al. /50/. The chromium-rich passive layer on super ferritic stainless steels was found to be stabilized by the addition of molybdenum and nitrogen, thus protecting the alloy from pitting attack /51-53/.

In the case of duplex stainless steel, the ferritic phase is generally immune to pitting attack due to the presence of higher chromium and molybdenum contents /31, 54/. Generally, the ferrite/austenite interfaces are preferred sites for initiation of corrosion in duplex stainless steels /55, 56/. Therefore, pits can form at these sites and, due to higher pitting corrosion resistance of the ferritic phase, grow into the austenitic phase. Nitrogen addition to duplex stainless steels has been reported to improve their pitting corrosion resistance /57/. Similarly, in this study it was found that the presence of 1200 ppm nitrogen in a duplex stainless steel increases the corrosion resistance.

The titanium present in the stainless steel could have played an important role in improving the localized corrosion resistance of type 316L stainless steel. Titanium improves the pitting corrosion resistance of titanium-modified stainless steel, where it is partially present in solid solution /58/. Titanium was considered to be helpful in forming TiS inclusions, which are insoluble in acids and prevent formation of MnS inclusions that are usually considered to be favorable sites for pit initiation in stainless steels /59/. Titanium may also play a prominent role in stabilizing the passive film, thus improving the pitting corrosion resistance /60/. During anodic polarization, titanium
dissolves along with other elements, including Cr, Fe, Ni and Mo, and diffuses into the Cr-rich mixed oxide passive film. The passive films on stainless steels have a high concentration of defects in bound water /61/. The competition between oxygen and chloride ions (from the electrolyte) adsorption onto the passive film surface is the underlying mechanism for the destruction of passivity. Pitting is initiated when specific adsorptions of chloride ions are favored over oxygen ions /62/. The presence of titanium in the passive film may reduce the defect concentration by occupying vacancies. Also, the adsorption of oxygen ions will be favored in preference to chloride ions. Hence, the protective film becomes stable with the addition of titanium.

Figure 12 compares the corrosion resistance characteristics of the various stainless steels studied under simulated body fluid conditions. In this figure, the resistance to pitting corrosion is expressed in terms of the breakdown

---

**Fig. 12:** A chart comparing the corrosion resistance characteristics of the various stainless steels studied under simulated body fluid conditions. Resistance to pitting corrosion is expressed in terms of the critical pitting potential ($E_p$), resistance to crevice corrosion is expressed in terms of the critical crevice potential ($E_{cc}$), and the safe region against corrosion attack represents the range from the corrosion potential ($E_{corr}$) to the protection potential ($E_p$).
potential ($E_a$), the resistance to crevice corrosion is expressed in terms of the critical crevice potential ($E_{cc}$), and the safe region against corrosion attack represents the range from the corrosion potential ($E_{cor}$ or OCP) to the protection potential ($E_p$). $E_{cor}$ is the potential of a corroding surface in an electrolyte relative to the reference electrode measured under open-circuit conditions. $E_p$ is the potential at which the reverse scan intersects the forward scan at a value that is less noble than $E_p$. The severity of crevice corrosion susceptibility increases with increasing hysteresis of the polarization curve, the difference between $E_a$ and $E_p$. The magnitude of this range is given as $\Delta E$ in Table 10. The super-ferritic stainless steel showed immunity to pitting and crevice corrosion attack and, hence, is not included in Fig. 12.

### 1.6.2 Crevice corrosion resistance

Crevice corrosion might occur in almost any multi-component 316L orthopaedic devices. This type of corrosion can cause sufficient clinical reaction to necessitate the removal of the implant /30, 63/. The susceptibility to crevice corrosion of the implant material can be determined by anodic polarization experiments. The critical crevice corrosion potential ($E_{cr}$) was thus determined in this work from anodic polarization curves as those shown in Figs. 13 and 14.

The presence of 680 ppm nitrogen in 316L stainless steel increased the $E_{cr}$ value from +272 mV (for reference 316L steel) to +459 mV, while the addition of 1600 ppm nitrogen raised it further to +730 mV. A similar influence of nitrogen addition on the critical crevice potential was also found for type 317L stainless steel containing 880 ppm and 1410 ppm nitrogen. The super-ferritic stainless steel was immune to corrosion attack even in the presence of crevice, while the $E_{cr}$ value for duplex stainless steel was as high as +972 mV. The titanium-modified stainless steel, however, exhibited crevice attack already at +332 mV, only a slight improvement in comparison to the reference 316L steel.

Based on the aforementioned results, the resistance of the different stainless steels to pitting corrosion may be ranked as follows: super-ferritic > duplex > 316L with 1600 ppm nitrogen > 317L with 1410 ppm nitrogen > 317L with 880 ppm nitrogen > 316L with 680 ppm nitrogen > Ti-modified 316L > reference 316L. With respect to crevice corrosion resistance, however, the order slightly changed: super-ferritic > duplex > 317L with 1410 ppm nitrogen > 316L with 1600 ppm nitrogen > 317L with 880 ppm nitrogen > 316L with 680 ppm nitrogen > Ti-modified 316L > reference 316L.
1.7 Modified stainless steels: a promising alternative to the currently used type 316L stainless steel for orthopaedic implants

Normal body fluids are known to exhibit an almost neutral pH (pH ~7.4). However, acidic conditions are often observed around implantation sites of bone fractures /64/. The pH in the early periods following surgery drops to the value of 4.0 and only in the course of 10 to 15 days attains neutrality. If wound healing is delayed, a lower pH will persist. The decrease in the pH and the chloride and other mineral ions in the body fluid at such critical sites might induce pitting corrosion. Moreover, the implant is subjected to weight bearing biomechanical forces, which result in bending and torsional stresses,
Fig 14: Potentiodynamic anodic polarization curves for reference 316L, Ti-modified 316L, super-ferritic, and duplex stainless steels.

as well as to cyclic loading. Thus, cracks may initiate around corrosion pits and propagate under stress corrosion cracking, corrosion fatigue, or fatigue failure modes /22, 65/.

In the present investigation, a pit-induced fatigue failure was observed in a compression bone plate (case no. 6), while a pit-induced stress corrosion cracking was noticed in an intramedullary nail the edges of which were severely pitted (case no. 7). Pitting and crevice corrosion induced corrosion fatigue fracture was observed in a Sherman bone plate (case no. 10). Two hip prostheses (cases no. 8 and 9) were also severely affected by pitting attack.
The pitting potential is considered as the criterion for evaluating the pitting corrosion resistance of materials. Moreover, the pitting corrosion resistance and the crevice corrosion resistance are interrelated. The increase in the pitting corrosion resistance is generally accompanied by an increase in the crevice corrosion resistance.

The pitting potential of an alloy is directly affected by the amount of passivating elements present in the alloy. A higher pitting corrosion resistance of an implant can be obtained by increasing the pitting potential of the implant alloy in the nobler direction. The modified steels adopted in this investigation, except Ti-modified 316L stainless steel, showed a very high pitting corrosion resistance compared to the currently used surgical 316L stainless steel. The super-ferritic, duplex, 316L with 1600 ppm nitrogen, and 317L with 1410 ppm nitrogen stainless steels all showed more than two-fold increase in the pitting corrosion resistance compared to the commonly used 316L alloy. The higher pitting corrosion resistance of these alloys may be attributed to the enrichment of chromium and the bound water in the form of OH⁻ ions at the outermost layer of the passive film.

1.8 Surface modification of stainless steels by ion implantation and bioeramic coatings

Surface coatings and barriers applied by techniques such as diffusion, electrodeposition, physical vapour deposition, chemical vapour deposition, cladding, etc., often impart satisfactory corrosion resistance to metals, which otherwise have inferior intrinsic properties. However, they have only limited use for protecting implants because they are often subjected to abrasion and wear, especially in orthopaedic implant applications. Ion implantation is a versatile surface alloying technique, which produces novel metastable solid solution surface alloys of no composition limits as those normally imposed by equilibrium phase diagrams. Moreover, nitrogen ion implantation can be carried out on finished orthopaedic devices, as the process does not create any dimensional changes at the surface after implantation. In addition to corrosion resistance, it also imparts excellent wear resistance to the modified surfaces.

1.8.1 Nitrogen ion implantation of stainless steels

Among the various ions implanted, nitrogen ion implantation is the most suitable technology for biomedical applications. Properties such as hardness.
corrosion resistance, wear, etc., can be improved without adversely affecting the bulk properties of the material /67/. This research has now reached the phase of technical maturity and can be effectively used to improve the overall performance of orthopaedic implant devices. Studies were undertaken to evaluate the corrosion resistance behavior of both reference and modified 316L stainless steels following nitrogen ion implantation. Nitrogen ions were implanted at different doses but fixed energy, and the implanted samples were subsequently subjected to electrochemical experiments to determine the optimum dose with respect to corrosion resistance under simulated body fluid conditions. Secondary Ion Mass Spectroscopy (SIMS) and X-ray Photoelectron Spectroscopy (XPS) were used to determine the elements depth profile and chemical state of the surface of the passive films on both implanted and non-implanted specimens. The objective of these analyses was to better understand the role of nitrogen in improving the passivity of nitrogen ion implanted specimens.

Nitrogen ion implantations were carried out at different doses ranging from $1 \times 10^{15}$ to $2 \times 10^{17}$ ions/cm$^2$ at 60 keV. Nitrogen ion implantation onto reference 316L stainless steel shifted the open circuit potential (OCP) to a nobler potential /68/. Implantation dose of $1 \times 10^{17}$ ions/cm$^2$ provided a uniform surface coverage of nitrogen and was found to be suitable for surface modification of orthopaedic implant devices. A two-fold increase in the breakdown and critical crevice potentials was observed for the nitrogen ion implanted specimen in comparison with the non-implanted reference 316L stainless steel. Accelerated leaching studies showed a minimal dissolution of the major alloying elements Cr, Ni and Mo from the surface of the specimen implanted at $1 \times 10^{17}$ ions/cm$^2$. This was attributed to the formation of a protective passive film by the implanted nitrogen /69/, which inhibited the further dissolution of alloying elements and broadened the passive range. The enhanced corrosion behavior, i.e., increase in the OCP, $E_b$, $E_p$ and $E_{oc}$ values may be related to the incorporation of nitrogen into the passive film and broadening of the passive region.

The non-implanted modified 316L stainless steel showed increased pitting and crevice corrosion resistance compared to the reference surgical grade. This enhanced localized corrosion resistance is attributed to the high Mo content and the low inclusion content in the modified steel. Nitrogen ion implantation improved even further the pitting and crevice corrosion resistances, the improvement being more pronounced as the ions dose increases. At a dose of $1 \times 10^{17}$ ions/cm$^2$, a three-fold increase in the localized
corrosion resistance was noticed. Accelerated leaching studies showed a minimization in leaching of alloying elements at a dose of approximately \(1 \times 10^{17}\) ions/cm\(^2\). SIMS depth profile studies showed that the outer surface became enriched with nitrogen. XPS studies showed that Fe, Cr and Mo were present in their respective oxides in the passive film on either non-implanted or implanted specimens, whereas Ni was found to be in its metallic form. The modified 316L stainless steel is by far more corrosion resistant than the currently used surgical grade. All of the above data thus indicated that this material should be considered as an attractive alternative to the currently used surgical grade 316L stainless steel.

1.8.2 Bioceramic coatings on 316L stainless steel

Bioceramic materials that are based on hydroxyapatite, \(\text{Ca}_{10} (\text{PO}_4)_6 (\text{OH})_2\) (HAP), the principal constituent of dentine, bone and other hard tissues, are considered promising for osseo-implants and as a means of aiding the regeneration of bone. There are indications that chemical bonding may occur between HAP and bone. However, the poor mechanical properties of HAP limit its use in implantation. Ceramic-coated metal implants for prosthetic applications provide the necessary porosity for bone ingrowth, while the underlying metal substrate bears the load, the full weight bearing capacity being attained soon after surgery. Thus, bioceramics play a dual role, both in preventing the release of metal ions (rendering it more corrosion resistant) and in making the metal surface bioactive.

Electrophoretic deposition of HAP on metal substrates, for example, has been used to achieve the uniform distribution of fine HAP deposits on the surface of type 316L stainless steel. This was carried out on 1 cm\(^2\) surfaces from a 2.5% suspension in isopropanol. The corrosion behavior of the HAP-coated steel was evaluated in vitro in Ringers solution simulated body fluid, exploring both DC and AC (Electrochemical Impedance Spectroscopy) techniques. Optimization of process parameters, including applied potential, deposition time, surface preparation, sintering conditions (namely, temperature and atmosphere – either air or vacuum) was carried out. These parameters were optimized based on the subsequent electrochemical behavior of the coatings. The optimal coatings were obtained at a coating voltage of 60 V, deposition time of 3 minutes, and subsequent vacuum sintering at 800°C for an hour.

A remarkable shift of the OCP, breakdown potential and electrochemical impedance parameters towards the noble direction was observed on
comparison with the uncoated steel. A decrease in capacitance and a marginal decrease in polarization resistance after cyclic polarization were observed in EIS experiments, indicating improved corrosion resistance. In general, higher values of impedance modulus ($|Z|$) and polarization resistance ($R_p$) and lower values of capacitance ($C$) were obtained by EIS when comparing the HIAP-coated steel to the uncoated steel. More detailed information on this work is given elsewhere [71]. The major conclusion was that HIAP coatings obtained by electrophoretic deposition may be considered for improving the corrosion resistance of type 316L stainless steel, and thus the biocompatibility, of implant devices.

**SUMMARY**

In the framework of this investigation, a survey of 50 failures of stainless steel implants revealed the occurrence of 42% fractured implants, 24% of implants that failed due to corrosion attack, 14% that failed due to onset of adverse tissue response, 6% that failed due to bending without fracture, 6% that failed due to severe wear, and 8% that cracked without catastrophic fracture. A classification of failures based on the anatomical location indicated that 74% of the failed implants were in the femoral area, 8% in the knee, 4% in the tibia, 2% in the humeral area and 6% in the radius and ulna. Moreover, about 91% of the multi-component devices had undergone visible crevice corrosion attack, the severity of which increased with the implantation period. Improvements in implant design, such as reducing the number of metal-metal interfaces or sealing the crevices with a polymeric gasket or a coating, can prevent most failures related to crevice corrosion.

Among the 10 selected cases that were studied in detail, in 4 cases the content of molybdenum was lower than that required by the ASTM reference, whereas in 5 cases the actual inclusion level was higher than the ASTM maximum level. Hence, poor material quality should be considered as an important factor in failures of orthopaedic implants; manufacturers should pay special attention to the requirements of ASTM specifications for surgical alloys. Yet, this may be enough only for reducing the risk of failure, but not for completely eliminating it.

The limited resistance of the reference 316L stainless steel against local (i.e., pitting and crevice) corrosion makes the selection of better alternatives highly desirable. The present study suggests that the super-ferritic (Sea-cure),
duplex (SAF 2205), 316L with 1600 ppm nitrogen, and 317L with 1410 ppm nitrogen stainless steels are all promising materials to replace the currently used 316L stainless steel surgical material; they all exhibit excellent pitting and crevice corrosion resistance. Nitrogen ion implantation and electrophoretic deposition of hydroxyapatite coatings should be considered as a viable alternative for improving the corrosion resistance of type 316L stainless steel and enhancing the biocompatibility of implant devices.

ACKNOWLEDGEMENTS

The authors acknowledge the research input from the collaborative research program between the Department of Analytical Chemistry, University of Madras (Chennai) and Indira Gandhi Centre for Atomic Research (Kalpakkam) on the subject of orthopaedic materials.

REFERENCES