BASIC SCIENCES

THE PROBLEM OF CORROSION IN ORTHOPAEDIC IMPLANT MATERIALS

D. Sharan

INTRODUCTION

Corrosion, the gradual degradation of materials by electrochemical attack, is a concern particularly when a metallic implant is placed in the hostile electrolytic environment provided by the human body (Litsky and Spector, 1994). Even though the freely corroding implant materials used in the past have been replaced with modern corrosion resistant superalloys, deleterious corrosion processes have been observed in certain clinical settings (Jacob et al, 1998).

HOW AND WHY IMPLANTS CORRODE

Two characteristics determine implant corrosion:

i) Thermodynamic forces, which cause corrosion (oxidation and reduction) reactions. These forces correspond to the energy required or released during a reaction (Jacobs, 1998). The electrochemical series links the normal electrode potentials of metals, usually in relation to hydrogen. Unfortunately, this series does not take into account the oxide film forming capability of these metals in any given electrolyte and it is more useful from the engineer's point of view to refer to the galvanic series in which metals are ranked in order of their relative reactivity in saline solutions (Atkinson and Jobbins, 1981).

ii) **Kinetic barriers to corrosion** which are related to factors that physically impede or prevent corrosion reactions from taking place (Jacobs, 1998). Only those metals, which have the capacity to form a protective oxide layer against corrosion can be used in orthopaedic implants. In order to limit oxidation, passive films must have certain characteristics. They must be non - porous and must fully cover the metal surface; they must have an atomic structure that limits the migration of ions and electrons across the metal oxide - solution interface; and they must be able to remain on the surface of the material even with mechanical stressing or abrasion, which can be expected in association with orthopaedic devices (Jacobs et al, 1998).

Address for Correspondence:

Dr. DEEPAK SHARAN
D.Orth, MS Orth, DNB Orth, MSc Orth Engg (Cardiff), Dip Orth Rehab Tech (Dundee)
Department of Orthopaedic Surgery
United Hospital, Kalapatti Road
Coimbatore-641 014, Tamilnadu, **INDIA**

CLINICAL IMPORTANCE OF THE PROCESS OF CORROSION

i) Corrosion can severely limit the fatigue life and ultimate strength of the material, leading to the **mechanical failure** of implant. There is a low but finite prevalence of corrosion - related fracture of the implant (Jacobs, 1998),

ii) The release of corrosion products may elicit an adverse **biological reaction** in the host, and several authors have reported increased concentrations of local and systemic trace metals in association with metal implants (Pazzaglia et al, 1986, Dorr et al, 1990). Although there is no specific histological evidence of the slow release of metal species that is thought to occur in association with all metal implants, accelerated corrosion and a tissue response (e.g., discolouration, foreign body response) that can be related directly to identifiable corrosion products have been demonstrated in the tissues surrounding multiple - part devices (Urban et al., 1994).

iii) Corrosion products have been implicated in causing **local pain and swelling** in the region of the implant, in the absence of infection (Park and Lakes, 1992).

iv) The presence of particulate corrosion and wear products in the tissue surrounding the implant may ultimately result in a cascade of events leading to **periprosthetic bone loss (** Urban et al, 1994).

v) **Excretion of excess metal ions** (especially chromium, cobalt and nickel) and their suspected role in induction of tumours e.g. malignant fibrous histiocytoma (Black, 1985). It remains to be proven whether the reports of tumours developing in the vicinity of metal implants are coincidental or otherwise. When the litany of documented toxicities **(metabolic, bacteriological, immunological or carcinogenic)** of these elements is considered, it should be emphasised that they generally apply to soluble forms of the elements and may not apply to the degradation products of prosthetic implants (Jacob et al, 1998)

CORROSION SUSCEPTIBILITY OF ORTHOPAEDIC IMPLANT MATERIALS

1. Stainless Steel : It contains enough chromium to confer corrosion resistance by passivity. The passive layer (chromium oxide) is not as robust as in the case of

Web version December 1999
IndiaOrth - the Indian Orthopedic Website - http://www.indiaorth.org

titanium or the cobalt - chromium alloys. The relatively resistant varieties of stainless steel are the austinitic types 316, 316L and 317, which contain Molybdenum (2.5 - 3.5%). Even these types of stainless steels are vulnerable to pitting and to crevice corrosion around screws, under certain circumstances such as in a highly stressed and oxygen - depleted region (Atkinson and Jobbins, 1981).

2. Cobalt chromium alloy : Both the cast and wrought varieties are passive in the human body and do not exhibit pitting, though moderate susceptibility to crevice corrosion may be observed (Black, 1988).

3. Titanium : It is a base metal (easily corroded) in context of the electrochemical series. However, it forms an adherent porous layer (Tio2) and remains passive under physiological conditions. Titanium implants remain virtually unchanged in appearance and offer superior corrosion resistance (Atkinson and Jobbins, 1981).

EXAMPLES OF THE VARIOUS TYPES OF CORROSION IN ORTHOPAEDIC IMPLANTS

I UNIFORM ATTACK

Definition : This refers to the inevitable corrosion to which all metals immersed in electrolytic solutions are condemned (Black, 1988).

Examples : Titanium - base alloys have lower overall corrosion rates compared to stainless steel and Cobalt chromium alloys. However, serum proteins can complex with chromium and nickel, increasing uniform attack by 2- to 10-fold (Black, 1988).

II GALVANIC CORROSION

Definition : Dissolution of metals driven bv macroscopic differences in electrochemical potentials, usually as a result of dissimilar metals in proximity (Jacobs et al, 1998).

Examples

1. Inappropriate use of metals, e.g., a stainless steel cerclage wire in contact with a cobalt or titanium - alloy femoral stem, a cobalt - alloy femoral head in contact with a titanium - alloy femoral stem, and a titanium - allov screw in contact with a stainless - steel plate (Griffin et al, 1983.

2. Due to cold - welding between instrument and implants. Using radioactive tracer techniques, Bowden and coworkers (1955) have shown that significant amounts of metal were transferred from screwdrivers to screw heads and from drill bits to plates.

3. Work - hardening and surface - finishing processes that produce plastic deformation generally make the deformed metal basic with respect to undeformed material of the same composition (Black, 1988). Compositional differences, either between parts because of manufacture from different master ingots within the same specification limits or because of deliberate mixing of metals, is the most likely cause of such effects (Black, 1988).

II FRETTING CORROSION

Definition : This describes corrosion occurring at contact areas between materials under load subjected to vibration and slip (Litsky and Spector, 1994).

Examples:

Repeated oscillatory motion is required, such as when multicomponent implanted devices are placed in weightbearing limbs or when the fixation achieved by a screw and plate construct is unstable. Cohen (1962) subjected plate - and screw assembles to cyclic stresses in saline solutions and found the greatest corrosions in the screw assemblies where the heads rubbed on the plate and where the nuts and washers were in contact. This is due to disruption of the passivation layer. Similar assemblies not subjected to the cyclical stresses did not show this marked effect.

III CREVICE CORROSION

Definition : This is a form of local corrosion due to differences in oxygen tension or concentration of electrolytes or changes in pH in a confined space, such as in the crevices between a screw and a plate (Bowden et al, 1955). The narrower and deeper the crack is, the more likely crevice corrosion is to start (Black, 1988).

Examples :

1. Recent retrieval studies have shown that 16 to 35% of modular total hip implants demonstrated moderate - to severe corrosion in the conical head - neck taper connections (Gilbert et al, 1993)

2. Studies of retrieved stainless steel multipart internal fixation devices show visible corrosion at the junction between screw head and the plate in 50-75% of all devices (Black, 1988).

3. Other typical crevices are scratches on the surface of an implant, the interface between bone and an implant, the cement - metal interface, and any other sharp interface likely to be depleted of oxygen relative to another oxygenated area (Pugh and Dee, 1988)

IV PITTING CORROSION

Definition : It is a form of localised, symmetric corrosion in which pits form on the metal surface (Black, 1988).

Examples :

i) Stainless steel is particularly predisposed to pitting corrosion due to inclusions of a dissimilar material trapped in the metal during a manufacturing process. These impurities may initiate pitting corrosion in relation to a grain boundary and thus can lead to component failure (Park and Lakes, 1992). It can also be initiated by scratches or handling damage (Black, 1988).

ii) Pitting was frequently observed in older stainless steel fracture fixation hardware, e.g., on the underside of screw heads (Black, 1988).

iii) It also occurs infrequently on the neck or the underside of the flange of proximal femoral endoprostheses (Black, 1988

V INTERGRANULAR CORROSION

Definition : This is a form of galvanic corrosion due to impurities and inclusions in an alloy (Black, 1988).

Examples :

1. Stainless steels, if improperly heat treated after fabrication, may corrode by this mechanism owing to a relative depletion of chromium from the regions near the grain boundaries. This phenomenon is called sensitisation (Black, 1988).

2. Welding of metals, which produces local melting and solidification, can also lead to a variant of this process, called knife - edge attack (Black, 1988).

VI LEACHING

Definition This form of corrosion results from chemical differences not within grain boundaries but within the grains themselves(Black, 1988

Examples : The presence of more than one phase in the alloy (multiphasic), e.g., 35% Ni containing cobalt-base alloy, F582.

VII STRESS - CORROSION CRACKING

Definition : It is a phenomenon in which a metal in a certain environment, especially those rich in chlorides, is subjected to stress and falls at a much lower level than usual as a result of corrosion (Greener and Lauten Schlager, 1971).

Examples

i) A straight fracture plate, when flexed, will experience a tensile stress on its convex surface and a compressive stress on its concave surface. This produces a difference in electrochemical potential, which renders, the convex surface anodic with respect to the rest of the plate. Corrosion, as an acceleration of uniform attack, or perhaps secondary tensile rupture of the passive film, will then attack the convex surface preferentially (Black, 1988).

ii) The same process will occur at stress risers in loaded devices, such as screw holes in fracture fixation plates or kinks in cerclage wire. In this case, the regions of higher stress, in the immediate vicinity of the stress risers, will corrode at the expense of the surrounding less stressed material (Black, 1988).

SUGGESTED MEASURES TO PREVENT CORROSION

Manufacturing Process

a) Surface treatment:

1. **Shot - peening or nitriding.** It has been recently shown that nitriding can reduce the magnitude of fretting corrosion of Ti-6AI-4V devices (Maurer et al, 1993).

2. **Implantation of ions** to harden the surface. This can improve the resistance to wear - accelerated corrosion phenomenon (Buchanan et al, 1987).

3. **Passivation** to thicken the protective oxide (Jacobs et al, 1998). Stainless steel forms a chromium oxide, a process that can be enhanced by chemical treatment with hot, concentrated nitric acid ("passivation"), boiling in distilled water or electrochemically (anodisation). Surgical stainless steel should contain 2.5-3.5% Molybdenum (Park and Lakes, 1992).

4. **Polishing** to remove asperities (Jacobs et al, 1998).

b) Quality control

1. **Improved standards and quality control.** The manufacturer should adopt the recommended metallurgical standards, fabricate the implants with care, and maintain adequate testing facilities

2. **Improvements in design** to minimise pits, crevices, large grain size, inclusions and porosity (Park and Lakes, 1992). Improved alloy 'cleanliness', especially the use of vacuum melting, and remelting, has largely eliminated pitting in such hardware (Black, 1988).

3. The **reduction of carbon to less than 0.03%** has virtually eliminated the risk of intercrystalline corrosion, which can occur when there is precipitation of chromium carbide at the grain boundary in stainless steel with a carbon content above this value (Park and Lakes, 1992). Unfortunately, lowering the carbon content results in lowering the ultimate tensile strength of stainless steel. Pitting corrosion inevitably occurs when a 304 steel is supplied instead of 316 (Atkinson and Jobbins, 1981).

4. **Proper heat treatment** after welding will restore the appropriate compositional distribution and prevent intergranular attack (Black, 1988).

5. **Avoiding implantation of different types of metal in the same region.** In the manufacturing process, matched parts from the same batch of the same variant of a given alloy must be provided. It must be ensured that instruments are made from the same material as the implant (Atkinson and Jobbins, 1981).

c) Research and development

1. **Development of alloy with good wear resistance and ability to repassivate at a high rate** (to prevent fretting)

2. **Coupling of two metals widely separated in the galvanic series,** e.g. Titanium and chromium, may not result in Galvanic corrosion but in enhancement of protection. The risk, however, is a potential increase of pitting or crevice corrosion (Atkinson and Jobbins, 1981).

3. Using an **alloy whose open circuit or rest potential lies below the critical potential for pitting** (Park and Lakes, 1992).

II EDUCATION OF THEATRE STAFF

1. The practice of **steam sterilization** of implants with saline in the environment gives rise to surface corrosion in both instruments and implants and should be **prohibited** (Mears, 1979).

2. Rough usage and scratches will break the oxide film on the surface of the implant and be the nidus where corrosion, especially stress corrosion, may start. Implants should be **handled with delicacy, never thrown around in basins,** or **shaken together in a basket,** or **immersed in saline.** Indeed, **implants should be kept in their packages or placed in protective containers** until the time of use.

3. **Prohibit reuse of implants** (if financially feasible). Implants become seriously attenuated after being subjected to repeated stresses in. the hostile environment of the body and are much more liable to fail with a second use. (Atkinson and Jobbins, 1981).

4. **Ensuring the instrument set matches the composition of implants.**

5. **Stringent quality control.** Severe cases of corrosion result either from the incorrect use of the materials or from the supply of material out of specification or in the wrong metallurgical condition (Atkinson and Jobbins, 1981*).*

III IMPROVED SURGICAL TECHNIQUE

1. Although it is a good general policy to **avoid mixing or "coupling" metals,** the only absolute contraindication appears to be the use of stainless steel as one component (Black, 1988). Thus stainless steel cerclage wires and screws should not be used with chromium - cobalt or titanium - base alloy implants (Park and Lakes, 1992). In clinical practice, it has been found that certain chrome-cobalt alloys can be used in combination with commercially pure Titanium and Ti-6AI-4V (Griffin et al, 1983).

2. **Avoiding transfer of metal from tools to the implant or tissue.** Drill guides should be used to prevent contact between drill and plate (Atkinson and Jobbins, 1981).

3. **Ensuring stable internal fixation,** according to AO/ASIF principles. Stenmann (1977) has demonstrated that an unstable fixation increases the likelihood of fretting corrosion by a factor of 100.

4. It should be recognised that a metal that resists corrosion in one body environment may corrode in another part of the body (Park and Lakes, 1992).

5. **Careful handling** of instruments and implants to prevent abrasions or cracking.

6. **Avoiding crevices due to poor implant assembly** (Atkinson and Jobbins, 1981).

CONCLUSIONS

It is important to realise that corrosion of orthopaedic blomaterials is not just an exercise in physics and chemistry. It is a pertinent clinical issue confronting all orthopaedic surgeons, irrespective of the location or the level of sophistication of their practice. While the need for stringent quality control on the part of indigenous implant manufacturers remains of paramount importance in the context of the Indian scenario, orthopaedic surgeons and other theatre personnel need to be made more aware to ensure that implants do not corrode and fail due to carelessness or ignorance.

REFERENCES:

1. Atkinson JR, Jobbins B. 'Properties of Engineering materials for use in the body In Dowson D, Wright V (eds). Introduction to the Biomechanics of Joints and Joint Replacement, London, Mechanical Engineering Publications Ltd, 1981
2. Black J. 'Metallic Ion Release and its relationship to Oncogenesis' In Fitzgerald RH Jr (ed): The Hip, St. Louis, Mosby, 1985: 199-213
3. Black J. 'Corrosion and degradation' In Orthopaedic biomaterials in research and practice, New York, Churchill, Livingstone, 1988: 235-266
4. Bowden FP, Williamson JBP, Laing PG. The Significance of Metal Transfer Orthopaedic Surgery. J Bone Joint 1955; 37B: 676-690
5. Buchanan RA, Rigney ED Jr, Williams JM. Ion implantation of surgical Ti - 6 Al - 4V for improved resistance to wear - accelerated corrosion, J Biomed Mater Res 1987, 21: 155 - 366
6. Cohen J. Corrosion testing of Orthopaedic Implants. J Bone Joint Surg 1962, 44A: 307-316
7. Dorr LD, Bloebaum R, Emmanual J, Meldrum R. Histologic, biochemical, and ion analysis of tissue and fluids retrieved during total hip arthroplasty. Clin Orthop 1990, 261: 82 - 95

8. Ferguson AB Jr, Laing PG. Corrosion and corrosion - resistant metals in Orthopaedic Surgery. Instr Course Lect, 1975; XV: 290 - 298
9. Gilbert TL, Buckley CA, Jacobs JJ. In vivo corrosion of modular hip prosthesis components in mixed and similar combinations. The effect of crevice, stress, motion and stress coupling. J Biomed Mater Res 1993, 27: 1533 - 1544
10. Greener EEL, Harcourt JK, Lauten Schlager EP. Material Science in Dentistry, Baltimore, Williams and Wilkins, 1972
11. Greener E, Lauten Schlager E. 'Materials for Bioengineering Applications' In: Brown JHV, Jacobs JE and Stuart L (eds) : Biomedical Engineering, Philadelphia, FA Davis, 1971
12. Griffin CD, Buchanan RA, Lemons JE. In vivo electrochemical corrosion study of coupled surgical implant materials. J Biomed Mater Res 1983; 17: 489 - 500
13. Jacobs JJ, Gilbert JL, Urban RM. Corrosion of metal orthopaedic implants. J Bone and Joint Surg, 1998; 8OA: 268 - 282
14. Litsky AS, Spector M. 'Biomaterials' In Simon SR (ed): Orthopaedic basic science, American academy of orthopaedic surgeons, 1994: 470 - 473
15. Maurer AM, Brown SA, Payer JH, Merritt K, Kawalec JS. Reduction of fretting corrosion of Ti - 6AI - 4V by various surface treatments. J Orthop Res 1993; 11: 865 - 873
16. Mears DC. Materials and Orthopaedic Surgery, Baltimore, Williams and Wilkins, 1979
17. Muller ME, Allgower M, Schneider R, Willenegger H. Manual of Internal Fixation, 3rd ed, Berlin, Springer-Verlag, 1991:14,95
18. Park JB, Lakes RS. 'Metallic Implant Materials' In Biomaterials - an Introduction, and ed, New York, Plenum Press, 1992:75-115
19. Pazzaglia UE, Minola C, Gualtieri G, Gualtieri, Riccardi C, Cecillani L. Metal ions in body fluids after arthroplasty. Acta Orthop Scand 1986; 57: 415 - 418
20. Pugh J, Dee R. 'Properties of Musculosk-eletal tissues and Biomaterials' In Dee R, Mango E, Hurst LC (eds); Principles of Orthopaedic Practice, New York, McGraw Hill, 1988
21. Steinmann SG; Corrosion of implants - in vivo and in vitro tests. Societe Europeenne pour les blomateriavx, 1977
22. Urban RM, Jacobs JJ, Gilbert JL, Galante JO. Migration of corrosion products, from modular hip prostheses. Particle microanalysis and histopathological findings. J Bone and Joint Surg 1994; 76A: 1345 - 1359