No corrosion of 304 stainless steel implant after 40 years of service

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When exposed to 0.9% NaCl type 304 stainless steel undergoes severe pitting corrosion within a matter of days. However, a Sherman plate fabricated from type 304 stainless steel remained inside a patient's arm for almost 40 years without any visible indications of corrosion. Given the previous understanding of the pathological environments this was considered quite remarkable. It is proposed that the low dissolved oxygen levels found in human-body fluids makes the long-term *in vivo* environment much more benign than would be anticipated from *in vitro* experiments. Furthermore, it is proposed that previous cases of localized pitting corrosion on stainless steel implants most likely arose due to the development of short-term aggressive conditions due to pathological changes in the surrounding tissue as a result of the trauma of the implant procedure. In the present case the Sherman plate was sufficiently small that the surrounding tissue was not aggravated sufficiently to lead to the development of such an environment aggressive. The conclusion that surgical implants are at most risk during the first few weeks of service implies that short-term corrosion protection methods, such as coatings, may be more effective than previously thought.

Introduction

The relative ability of different grades of stainless steels to resist pitting corrosion in a chloride environment can be ascertained from their respective pitting resistance numbers (PREN), which is defined as:

$$\text{PREN} = \%\text{Cr} + (3.3 \times \%\text{Mo}) + (16 \times \%\text{N})$$

For example a typical 316L stainless steel (17% Cr, 8% Ni, 2% Mo, balance Fe) would have a PREN of 23.6 whereas the less corrosion resistant type 304L stainless steel (18% Cr, 8% Ni, balance Fe) only has a value of 18.

The compositions of body-fluids are complicated, however, from the perspective of corrosion the most important characteristics are the chloride, dissolved oxygen and pH levels. A 0.9% NaCl solution is considered to be isotonic with blood and under normal conditions most body-fluids have a pH of 7.4 and a temperature of 37 °C. In these respects body-fluids appear to be slightly less aggressive than seawater. This is consistent with the findings of Zitter [1] who after surveying a number of corrosion related problems over a 10-year period recommended that a PREN of greater than 26 should be used for surgical implants, whereas a value of 40 is usually recommended for stagnant seawater. A PREN requirement of 26 makes the typical 316L stainless steel a marginal material and this is consistent with the findings of Scales *et al*. [2], who in 1959 reported that 24% of the type 316 stainless steel bone plates and screws removed from patients showed evidence of crevice corrosion. Both pitting and crevice corrosion have previously caused the premature removal of 316L stainless steel implants [3, 4]. To compensate for this high nitrogen and ultraclean (e.g. 316LVM) stainless steels have been developed [5].

As stated above the PREN value for most 304L stainless steels is only 18, hence it is not surprising that this material has been found to be unsuitable for use in surgical implants [6, 7]. Indeed the mistaking use of 304L screws, instead of ones of 316L has caused a number of failures [8]. Therefore it would be surprising if 304 stainless steel implants were to be recovered without any signs of corrosion. However, this paper reports such a case, and what is more the recovered Sherman plates and screws had been implanted for almost 40 years.

Experimental

The patient who was born in 1947 and worked as a postman had previously fractured both his right ulna and radius at the mid-shaft region in a road traffic accident.

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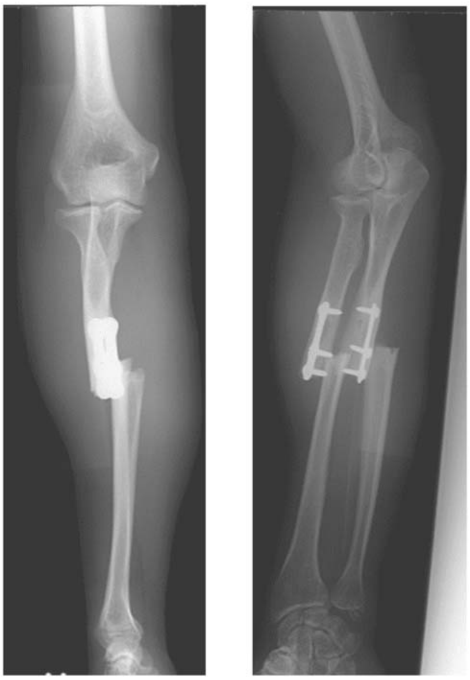

Figure 1 Radiograph showing fractures of both forearm bones, at the distal screws of the plate fixation.

This was in about 1960, where both fractures were reduced with bone plates and screws. He was 13 years old then. In 1998, he again fractured his right radius and ulna in another road traffic accident. Both fractures were at the distal screws of the plate fixation (Fig. 1). There was minimal bone growth over the proximal part of one plate, but there was no evidence of growth over the majority of the plates' surfaces or the screws, such growth, if it had existed, could have protected the implant from corrosion (Fig. 2). The old plates were removed, after being *in situ* for about 38 years, and the fracture reduced with two new plate implants. No inflammation or black material in the soft tissue surrounding the original implant was noted. The implants were 4-cm three-hole bone plates, each with three 3-mm diameter screws, 14-mm in length. Both plates and their respective screws were removed intact. The condition of the plates were remarkably good, with just a few scratches which were obtained during retrieval and the

Figure 3 Close-up of the removed plate, showing that no corrosion appeared on the plate. The manufacturer's name ''DOWN.A'' was still clearly readable.

manufacturer's name ''DOWN.A'' was still clearly visible (Fig. 3). The surgeon who removed the plate and screws was sufficiently impressed to enquire why it was that not all implants were made of such highly corrosion resistant alloys.

The plates and screws were examined under a scanning electron microscope (SEM). Elemental analysis was preformed by both an energy dispersive X-ray (EDX) attachment on the SEM and by proton induced X-ray emission (PIXE) using a nuclear microscope. Full details of the nuclear microscope and the PIXE technique have been published elsewhere [9], it is sufficient to say

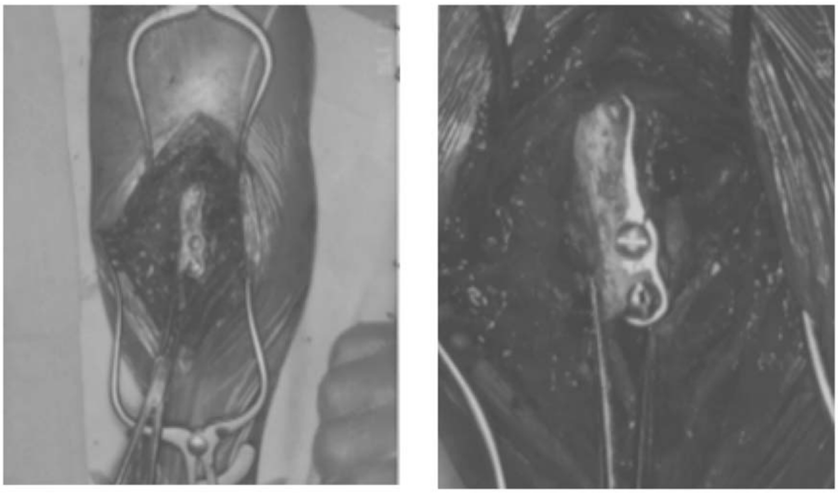

Figure 2 Photographs showing minimal bone growth over the proximal part of one plate, with no evidence of growth over the majority of the plates' top surface.

that the technique is recognized as being more reliable than EDX and X-ray fluorescence spectroscopy (XFS).

Results and discussion

Examination of the plates and screws under the SEM confirmed the absence of any pitting corrosion, even in the countersink regions, which would have formed crevices with the screw heads. The elemental analysis data from both the EDX and PIXE are shown in Table I, whilst Fig. 4 shows the EDX spectra of both the screws and plates. In all the important aspects there was good agreement between the two analysis techniques. Although the compositions of the plates were different from that of the screws there were no significant variations between the six screws or between the two plates. The most striking thing about the data is the absence of molybdenum in the Sherman plates; in fact, this was the reason for doing the PIXE analysis as it was first thought the EDX data must be incorrect. Table I shows that the screws appear to have been fabricated from grade 316 stainless steel with a PREN of about 26.5, just sufficient to prevent corrosion, whereas the plates were manufactured from grade 304 stainless steel with a PREN of only 18.5, significantly below the 26 recommended by Zitter [1]. Given that in combinations of grades 304 and 316 stainless steels usually result in accelerated corrosion of the former [8], the data reported in Table I clearly begs the question of why did the plates not corrode?

Pitting corrosion occurs if the open-circuit potential of a metal rises above a critical value known as the pitting potential (Ep). The open-circuit potential of passive metals, such as stainless steels, is strongly dependent on the redox potential of the surrounding environment, that is to say that the more oxidizing the environment the more positive the open-circuit potential. Usually the most important oxidizing agent in aqueous solutions is dissolved oxygen and from the work of Wang *et al*. [10] it can be determined that in an aerated solution of 0.9% NaCl at 37 °C pitting would initiate on 304 stainless steel within about 5 days. However, the dissolved oxygen levels in human blood are lower than saline solutions exposed to air atmospheres, by a factor of slightly less than two for arterial blood and a factor of about four for venous blood (Table II) [11]. Therefore the long-term open-circuit potentials adopted by *in vivo* stainless steel

TABLE I Composition of plates and screws as determined by EDX and PIXE (wt %)

	Fe	Cr	Ni	Mo	Mn
EDX					
Plates	66.1	18.7	12.7	0.0	1.5
Screws	64.6	17.2	13.3	2.8	1.4
PIXE					
Plates	71.0	18.4	10.2	0.0	0.5

TABLE II Comparison of oxygen and carbon dioxide levels in real and simulated human body-fluids according to Moxham and Costello [11]

	PO_2 (mm Hg)	PCO_2 (mm Hg)	HCO_3^- mmol dm^{-3}
Artery blood	85–100	35–45	25
Vein blood	40	42–48	25
NaCl solution	160	2	—

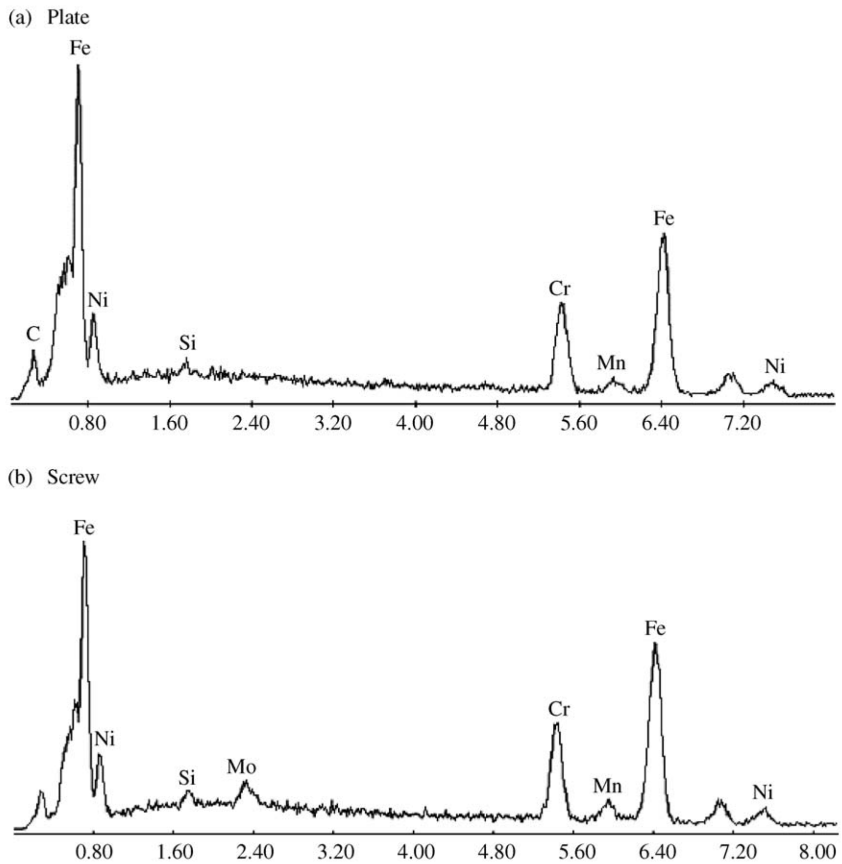

Figure 4 EDX spectra collected from (a) plate and (b) screw. There were no significant variations between the six screws or between the two plates.

implants should be negative of values determined in any external *in vitro* experiments, and apparently sufficiently so in the present case to prevent the initiation of localized pitting or crevice corrosion.

However, it is well known that surgical operations plus the presence of the implant themselves may cause the surrounding tissue to undergo severe pathological changes that result in the development of a more corrosive environment [12]. Laing reported that the pH around a newly inserted surgical implant can drop to as low as 4.0, due to the build-up of haematomas, a condition that could last several weeks [1, 13]. Hydrogen peroxide may also be generated during the initial stages of the inflammatory response of the surrounding body tissue after insertion of an implant [14, 15]. Any decrease in the pH of the local environment greatly increases the likelihood of pitting corrosion and as H_2O_2 is a powerful oxidizing agent, so its presence would push the open-circuit potential positive, again increasing the changes of the pitting. Very recently Kocijan *et al*. [16] have shown that the presence of proteins reduces the pitting potential of 304L stainless steel physiological solutions, apparently by several hundred millivolts. Increased protein levels have been reported to exist throughout the reparative phase of the callus, particularly in fibrous tissue, and in proliferating chondrocytes, osteoblasts, and immature osteocytes [17]. Therefore a stainless steel implant is at most risk from pitting corrosion in the period immediately after insertion.

It is known that the extent to which the pathological changes occur depend on the size and shape of the implant [18] and thus the severity of the risk of pitting corrosion will also depend on these factors. Compared to many other implants the Sherman plates recovered from the patient in the current investigation were small (only 4 cm long and about 0.1 cm thick) and flat and thus probably do not aggravate the surrounding tissue to a large extent [19, 20]. Therefore, the resultant fall in local pH and rise in H_2O_2 and protein concentrations were either too small to cause the open-circuit potential of the 304 stainless steel implant to exceed its pitting potential or if the pitting potential was exceeded, the aggressive conditions did not last long enough for pits to initiate, induction periods for pitting of a few days, or even weeks, being common.

Conclusions

A Sherman plate fabricated from type 304 stainless steel performed its required task inside a patient's arm for almost 40 years without any visible indications of corrosion. Given the previous understanding of the pathological environments this was considered quite remarkable, especially as there have been many incidences of more resistant alloys suffering corrosion under similar circumstances. It is proposed that the low dissolved oxygen levels found in human-body fluids makes the long-term *in vivo* environment much more benign than would be anticipated from *in vitro* experiments. Furthermore, it is proposed that previous cases of localized pitting corrosion on 304 and 316 stainless steel implants [1, 6] most likely arose due to the development of short-term (weeks) locally aggressive conditions (low pH, H_2O_2 production, high proteins levels) due to pathological changes in the surrounding tissue as a result of the trauma of the implant procedure. In the present case the Sherman plate was sufficiently small that the surrounding tissue was not aggravated sufficiently to lead to the development of an environment aggressive enough to cause pitting of 304 stainless steel. The current case clearly bares testament to the importance of the pathological changes that accompany the healing process after surgery in considering the corrosion of implants. Furthermore, the conclusion that surgical implants are at most risk during the first few weeks of service implies that short-term corrosion protection methods, such as coatings, may be more effective than previously thought.

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