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

D. J. BLACKWOOD1,*, B. P. PEREIRA2
1Department of Materials Science, Department of Orthopaedic Surgery, National University of Singapore, Kent Ridge, Singapore 119260, Republic of Singapore
E-mail: masdjb@nus.edu.sg
2Musculoskeletal Research Laboratories, Department of Orthopaedic Surgery, National University of Singapore, Kent Ridge, Singapore 119260, Republic of Singapore

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.
© 2004 Kluwer Academic Publishers

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 mistaken 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.

*Author to whom all correspondence should be addressed.
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 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...