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Compatibility of ferritic and duplex stainless steels as implant materials: *in vitro* corrosion performance

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The pitting corrosion, crevice corrosion and accelerated leaching of iron, chromium and nickel of super-ferritic and duplex stainless steels, and for effective comparison the presently used 316L stainless steel, have been studied in an artificial physiological solution (Hank's solution) by the potentiodynamic anodic polarization method. The results of the above studies have shown the new super-ferritic stainless steel to be immune to pitting and crevice corrosion attack. The pitting and crevice corrosion resistances of duplex stainless steel were found to be superior to those of the commonly used type 316L stainless steel implant materials. The accelerated leaching study conducted for the above alloys showed very little tendency for the leaching of metal ions when compared with 316L stainless steel. Thus the present study indicated that super-ferritic and duplex stainless steels can be adopted as implant materials due to their higher pitting and crevice corrosion resistance.

1. Introduction

Metals are often chosen as implant materials because of their inherent mechanical properties. Currently the surgical implants are usually made of one of three types of material: austenitic stainless steels, cobalt–chromium alloys and titanium and its alloys [1]. Amongst all these materials the austenitic stainless steels, especially type 316L stainless steels, are the most popular ones because of their relatively low cost and reasonable corrosion resistance [2]. However, it has been reported that type 316L stainless steel orthopaedic implants frequently become corroded and degraded, and release iron, chromium and nickel ions into the human body [3]. The chromium and nickel ions thus released have been shown to be powerful allergens and are demonstrated to be carcinogenic in rats [1].

The artificial mechanical devices that are implanted into the human body are considered to have failed when they are prematurely removed from the body, as the implant does not accomplish its intended function and hence has to be removed due to the implant failure [3]. Therefore a high corrosion resistance is demanded for implants to obtain biocompatibility and acceptability. Failure investigations and surveys of failed stainless steel implants removed from human subjects have revealed significant localized corrosion attack, namely, pitting [4, 5] and crevice corrosion [6, 7], which are the most frequently observed types of corrosion attack. It has been reported that the pits can act as sites for fatigue cracks and stress corrosion cracks to develop [4, 5]. The above factors have necessitated the development of stainless steel implant materials with a high resistance to localized corrosion attack and crack propagation.

The widely used austenitic stainless steels containing 8% nickel have been demonstrated to exhibit reduced cracking resistance in chloride solution [8]. The cracking resistance will be greatly improved if the nickel content of the stainless steel is decreased and the microstructure changed from the austenitic phase to a mixture of ferritic and austenitic phase (duplex stainless steels) or a fully ferrite phase (ferritic stainless steels). The presence of a ferrite phase in duplex and ferritic stainless steels will inhibit the crack propagation and pit initiation [9]. The objectives of the present study were to evaluate the corrosion behaviour of previously untried ferritic and duplex stainless steels in simulated body conditions, and the possibility of adopting them as orthopaedic implant materials.

The *in vitro* anodic polarization study is a standard test for the determination of pitting and crevice corrosion resistance of metallic implant materials [10]. However, the polarization study is only a qualitative test to determine the corrosion resistance of an implant alloy [11]. In the case of implants, there is a need for the quantitative determination of corrosion products because of their adverse effects on the human body. An accelerated leaching study by a chronoamperometric method has been used to gather quantitative information on the corrosion products [12]. In this method, the corrosion process can be accelerated by imposing an anodic potential in the passive region of the metallic implant material, and thus the simulation of a long time of contact between the implant and a normal biological medium is achieved in a reduced

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time. In the present study *in vitro* corrosion behaviour was studied on a new super-ferritic steel (Sea-cure, a product of Colt Industries) and a duplex stainless steel (Sandvik, SAF 2205) by means of electrochemical methods. The pitting and crevice corrosion resistance were evaluated and their performance in accelerated leaching under simulated conditions were assessed.

2. Experimental procedure

2.1. Electrode preparation

The chemical compositions of the super-ferritic, duplex and 316L stainless steels are given in Table I. Sheet materials in the as-received solution-annealed condition were used in the present investigation. The alloys were cut to 1 cm × 1 cm × 0.3 cm size and soldered to a copper rod to provide electrical contact. Samples were then doped with epoxy resin in such a way that only one side with 1 cm^2 surface area was exposed, and this formed the working electrode. In order to avoid the need for severe polishing after the resin mounting (which might cause microcracking at the metal–resin interface), the specimens were wet-ground with SiC papers down to 600 grit followed by 5 and 1 μm diamond paste before mounting. The edges of the mounted specimens were examined with a 100X (oil immersion) objective lens in an optical microscope for the appearance of any gap between the metal and epoxy resin. If any gap was seen, the specimens were remounted. The electrodes were then ultrasonically cleaned for 3 min and passivated in a solution of 30 vol % HNO_3 at 60 °C for 30 min, thoroughly washed in deionized water, rinsed in alcohol and dried.

2.2. Polarization cell assembly

A three-compartment electrochemical cell (borosilicate glass) with a capacity of 500 ml was adopted. Platinum foil was used as the counterelectrode and a saturated calomel electrode (SCE) was used as the reference electrode. The electrolyte used was Hank's solution (whose composition is shown in Table II) and its pH was adjusted to 7.00 ± 0.05 with sodium bicarbonate and maintained at 37 ± 1 °C by means of a thermostatted water bath. The test solution was continuously purged with nitrogen; the working electrode was then introduced into the cell and the potential was allowed to stabilize for 20 min.

2.3. Pitting corrosion

In the anodic polarization study, the potential was increased in the noble direction at a rate of 0.166 $mV\,s^{-1}$ until the breakdown potential (E_b) was attained where the alloy entered the transpassive or pitting region. The sweep direction was then reversed after reaching an anodic current density of 0.5 $mA\,cm^{-2}$ until the reverse scan reached the passive region. The potential at which the reverse anodic scan meets the passive region is the pit protection potential (E_p).

TABLE I Chemical composition of stainless steels (wt %)

	Cr	Ni	Mo	Ti	Co	Al	C	N
Super-ferritic	27.16	2.06	3.36	0.54	0.13	0.08	0.021	0.027
Duplex	21.8	5.2	3.1	–	–	–	0.02	0.12

TABLE II Composition of artificial physiological solution (Hank's balanced salt solution)

Compound	Concentration ($g\,l^{-1}$)
NaCl	8.00
$CaCl_2$	0.14
KCl	0.40
$NaHCO_3$	0.35
Glucose	1.00
NaH_2PO_4	0.10
$MgCl_2 \cdot 6H_2O$	0.10
$Na_2HPO_4 \cdot 2H_2O$	0.06
$MgSO_4 \cdot 7H_2O$	0.06

The parameters of interest that were recorded during the cyclic potentiodynamic polarization tests were (i) the corrosion potential E_{corr}, (ii) the pitting potential E_b, (iii) the pit protection potential E_p, and (iv) the safe region for corrosion attack (ΔE).

2.4. Crevice corrosion

A glass assembly was designed as described by Dayal *et al.* [13] to create a crevice on the mounted electrodes. The tip of a glass rod was brought into close contact with the electrode surface using a nut and threaded rod arrangement. The angle between the glass and the electrode surface was maintained at 1.2 ± 0.2 °. To determine the critical crevice potential (E_{cc}), the potential was increased in the noble direction at a rate of 10 $mV\,min^{-1}$ until E_{cc} was attained where the alloy entered the transpassive region. To rule out any possibility of pitting and edge attack on the electrode surface soon after the experiment, the electrode surface was thoroughly examined in an optical microscope. The electrodes with edge attack were rejected and those electrodes without edge attack were taken into consideration for the study.

2.5. Accelerated leaching of iron, chromium and nickel

In the accelerated leaching study, the working electrodes were immersed in Hank's solution and allowed to stabilize at constant potentials of +200, +300, +400 and +500 mV and at E_b for 1 h in 100 ml of the test solution. At the end of each experiment, the chemical composition of the test solution was analysed by inductively coupled plasma atomic emission spectrometry, and the data were compared with the compositions of the steels listed in Table I.

3. Results and discussion

3.1. Critical pitting potential

The critical pitting potentials of the ferritic, duplex and 316L stainless steels were determined from the polarization curves shown in Fig. 1. The ferritic stainless steel exhibited passivity up to + 1120 mV, and beyond this potential transpassive dissolution took place without pitting on the specimen. The immunity of the alloy to pitting attack may be attributed to the presence of chromium, molybdenum, nitrogen and titanium in the passive layer. A chromium-rich passive film becomes stabilized with the addition of the above alloying elements and protects the alloy from pitting attack. Molybdenum forms a thin protective molybdenum oxide film and provides an impervious layer for the passive film to develop.

The mean value of the critical pitting potential (E_b) for the duplex stainless steel was +1189 mV, whereas type 316L stainless steel showed a pitting attack at +365 mV. Thus the pitting potential of duplex stainless steel was found to be nobler than that of the currently used type 316L stainless steel. This study indicated that the initiation of corrosion pits in duplex stainless steel is hindered in simulated body conditions.

The ferrite phase of duplex stainless steel is generally immune to pitting attack due to the presence of a higher level of chromium and molybdenum [2]. Generally, the ferritic and austenitic phase boundaries are defective areas in duplex stainless steels, so pits can form at these sites and due to the higher pitting resistance of the ferritic phase the pits will grow into the austenitic phase. The addition of nitrogen to duplex stainless steel has been reported to improve the pitting resistance [14]. In the present study, the presence of 1200 p.p.m. of nitrogen in the duplex stainless steel increased the pitting resistance of austenitic phase as explained by the following points. If the pit grows in the austenitic phase, the conditions prevailing at that pit site have been reported to be similar to those of the active dissolution state. In general, during active dissolution, alloying elements such as iron, chromium and nickel dissolve whereas non-active elements such as nitrogen can enrich at such a surface. Such a segregation has been reported by Newman *et al.* [15] and also by Clayton and Martin [16], to at least a level of seven times the original concentration of nitrogen present in the alloy. This stage leads to the formation of ammonium ions and subsequently nitrogen compounds at the pits, which increase the pH and slow down the pit growth kinetics, or it may provide an inactive layer to improve the pitting corrosion resistance.

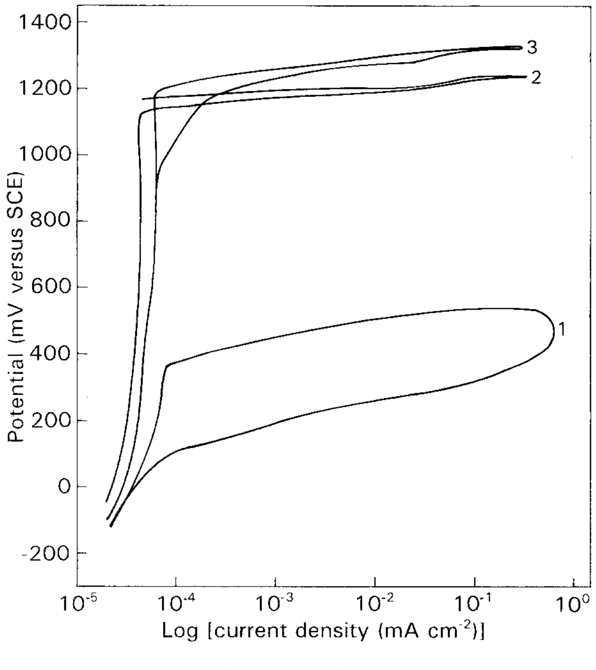

Figure 1 Potentiodynamic anodic polarization curves for (1) type 316L, (2) super-ferritic and (3) duplex stainless steels.

3.2. Pitting protection behaviour

The pit protection potential was determined for the alloys from the polarization curves shown in Fig. 1. New pits cannot be formed above this potential and existing pits will not grow below this potential. The difference between the pit protection and corrosion potentials is referred to as the relative corrosion resistance (ΔE). Super-ferritic stainless steel did not show any pitting attack up to +1120 mV, and beyond this potential transpassive dissolution was observed. During the reverse scan, the pit protection potential was also found at the same potential, +1120 mV. This indicated the superior resistance of super-ferritic stainless steel towards pitting initiation and growth. The mean value of pit protection potential for the alloy duplex stainless steel was +950 mV, whereas for type 316L stainless steel it was +24 mV. The mean value of ΔE for super-ferritic stainless steel was 1132 mV and for duplex stainless steel it was 1034 mV. However, for the type 316L stainless steel it was 132 mV. The higher value of ΔE for the super-ferritic and duplex stainless steel reflects an enhanced resistance to pitting corrosion compared to the commonly used type 316L stainless steel.

3.3. Critical crevice potential

Crevice corrosion (corrosion between screws and a plate or other contacting areas) occurs in almost all multicomponent 316L stainless steel orthopaedic devices, and this type of corrosion can cause sufficient clinical reaction to necessitate the removal of the implant [7].

The critical crevice potentials (E_{cc}) of super-ferritic, duplex and 316L stainless steels were determined from the polarization curves shown in Fig. 2. The super-ferritic stainless steel showed immunity to corrosion attack even in the presence of crevices. The mean value of the critical crevice potential for duplex stainless steel was +972 mV, whereas for 316L stainless steel it was +272 mV. Thus it is evident that the duplex stainless steel exhibited higher E_{cc} value with improved crevice corrosion resistance under simulated body conditions.

The pH of the normal body fluid is 7.4. In this

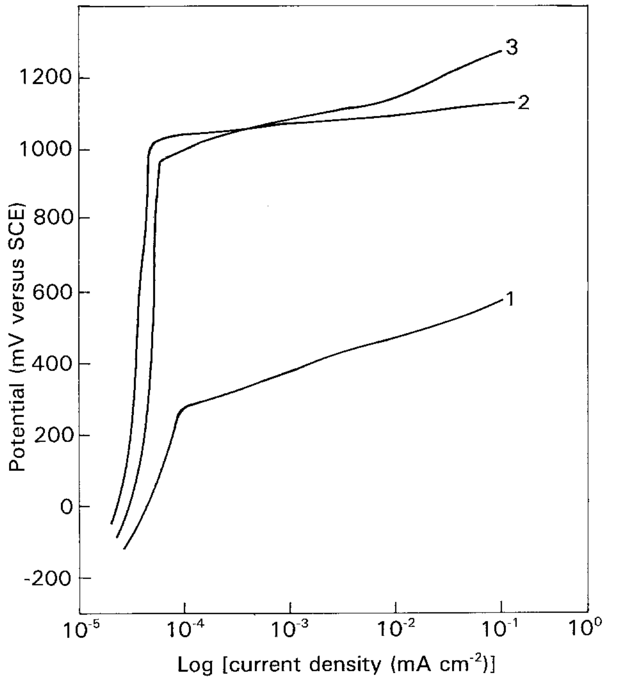

Figure 2 Potentiodynamic anodic polarization curves for (1) type 316L, (2) super-ferritic and (3) duplex stainless steels in the presence of a crevice.

condition, oxygen is the principal depolarizer and oxygen present at the implant crevice is consumed quite rapidly, either in the cathodic reaction or for passivation. This inhomogeniety in oxygen concentration leads to the formation of a concentration cell. However, the change in the pH of the medium seems to be of greater importance than the change in the oxygen concentration [17]. Acidification of the crevice area can take place as a result of anodic reaction:

$$M + H_2O \rightarrow MO + 2H^+ + 2e^-$$

This acidification can accelerate the anodic reaction in the crevices [17]. The presence of nitrogen in duplex stainless steel improved the crevice corrosion resistance due to the formation of ammonium ions at the pits present in the crevices, which increased the pH and slowed down the pit growth kinetics:

$$N + 4H^+ + 3e^- \rightarrow NH_4^+$$

Clayton [18] suggested a chemical rather than an electrochemical mechanism for the formation of ammonium ions, so that the pH was controlled by the formation of nitrides formed from the anodically segregated nitrogen. Kamachi Mudali *et al.* [19] reported that the dissolution of nitrogen at the pit site, and the subsequent formation of ammonium ions and nitrate compounds, improved the pitting corrosion resistance. Thus the effect of a localized decrease in pH at the crevice area can be avoided by using duplex stainless steel as an implant material.

3.4. Accelerated leaching in simulated body conditions

In the accelerated leaching study the concentrations of metal ions, namely iron, chromium and nickel, present in the test solution after ageing for 1 h were determined and the results are illustrated in Figs 3, 4 and 5,

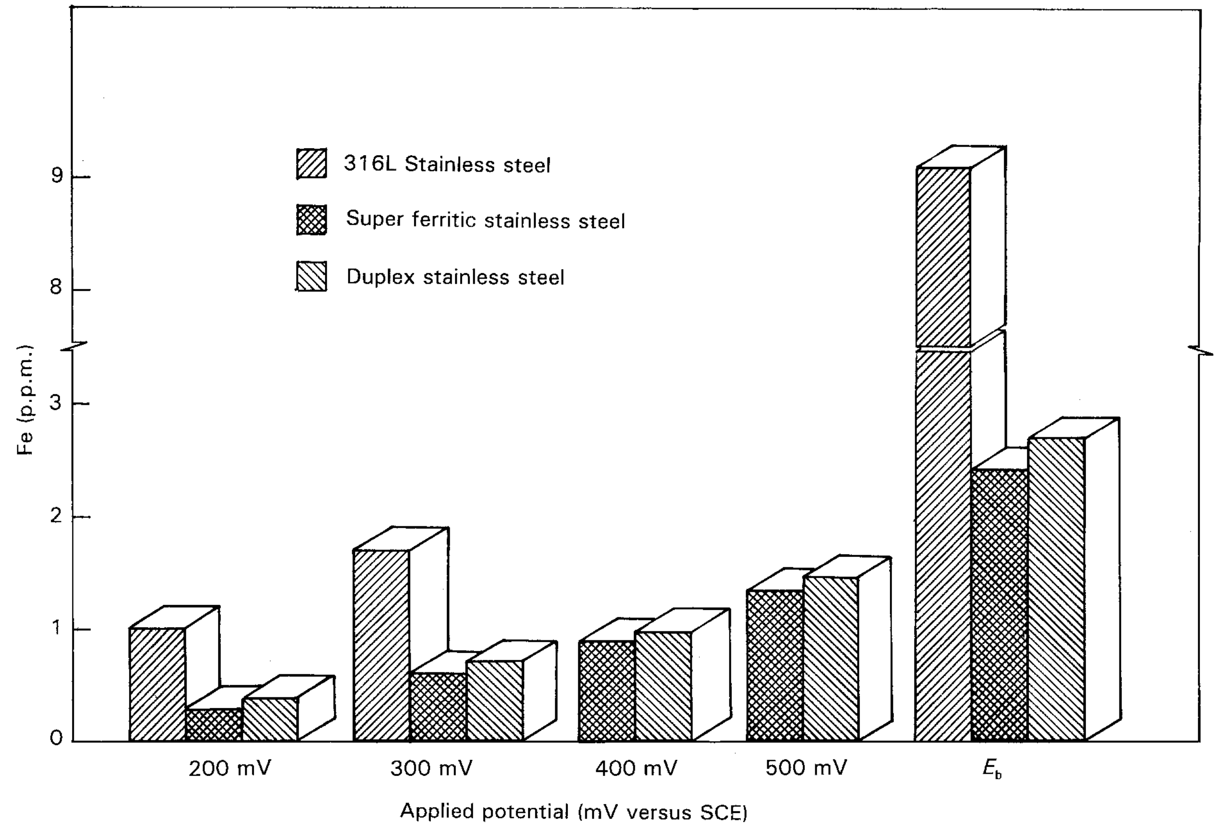

Figure 3 Concentration of iron present in the solution after the accelerated leaching of type 316L, super-ferritic and duplex stainless steels at different imposed electrode potentials.

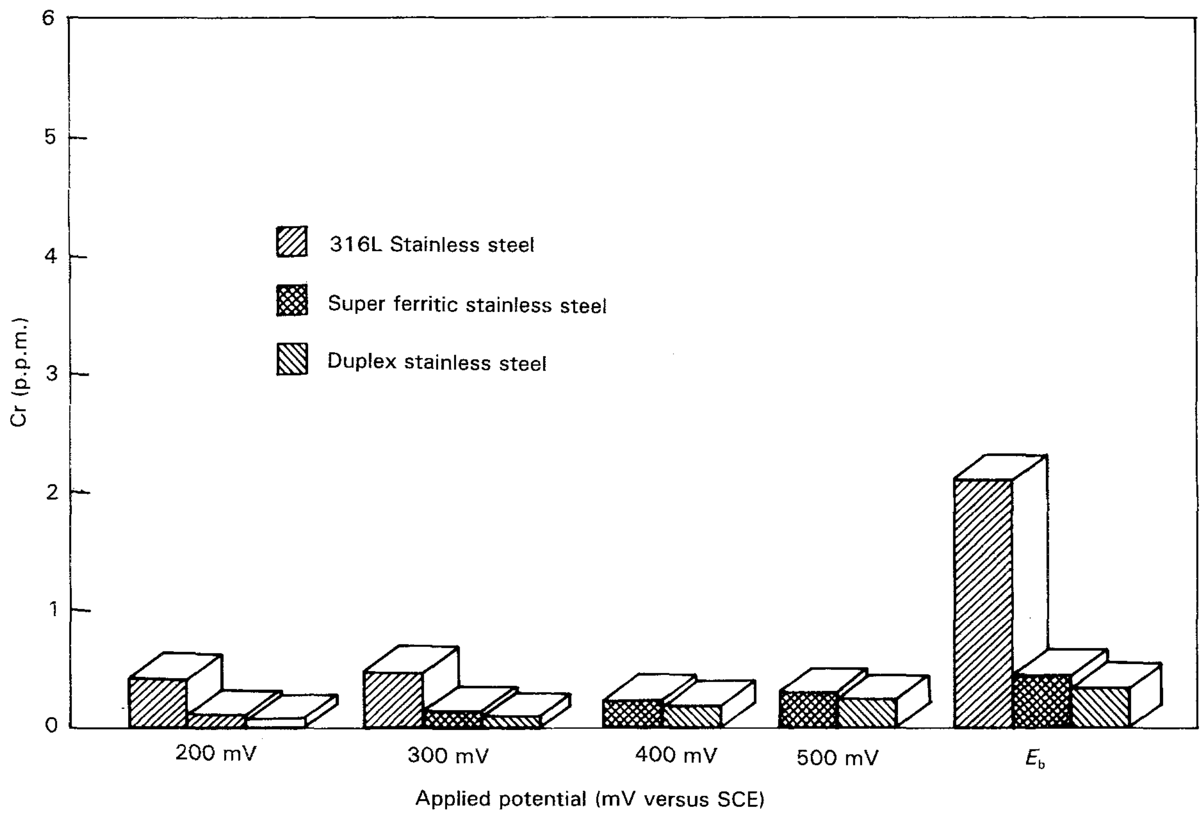

Figure 4 Concentration of chromium present in the solution after the accelerated leaching of type 316L, super-ferritic and duplex stainless steels at different imposed electrode potentials.

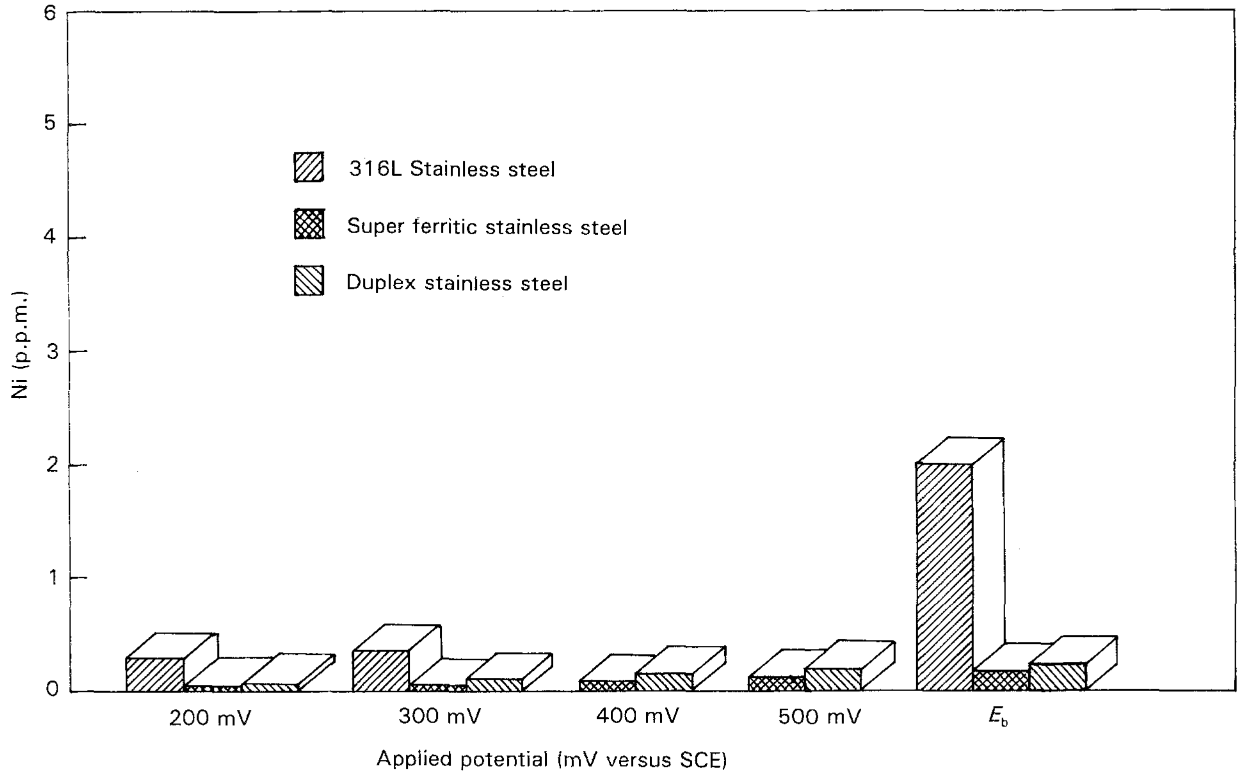

Figure 5 Concentration of nickel present in the solution after the accelerated leaching of type 316L, super-ferritic and duplex stainless steel at different imposed electrode potentials.

respectively. It is seen that significant amounts of metal ions were released into the solution, even in the passive region, for type 316L stainless steel implant material.

Ferritic and duplex stainless steels showed very little tendency for the leaching of metal ions compared to type 316L stainless steel at imposed potentials of +200, +300, +400 and +500 mV. Pitting attack occurred at +365 mV and hence the leaching study was not conducted at +400 and +500 mV.

The amounts of metal ions released from duplex stainless steel at imposed potentials of +200 to +500 mV were lower than for ferritic stainless steel. It has been reported that enrichment of nitrogen takes place at the passive film–metal interface [15]. Such enrichment could have strengthened the interface and impeded the release of metal ions through the passive film [15]. The presence of nitrogen in this alloy reversibly impedes active dissolution in the passive region. This may indicate the occurrence of a cross-over of the rates of metal dissolution (anodic) and nitrogen dissolution (cathodic) due to an enrichment of nitrogen atoms at the interface [20].

Thus at the pitting potential, type 316L stainless steel showed an enhanced leaching of the metal ions iron, nickel and chromium, whereas the super-ferritic and duplex stainless steel showed a very low leaching of metal ions.

3.5. Environment of implanted materials in fractured bone sites

Though normal body fluids are at neutral pH (7.4), an acidic condition has been reported at the implanted site of a bone fracture [20]. The pH in the early periods following surgery drops to 4 and only in the course of 10 to 15 days does it attain neutrality. If wound healing is delayed then a lower pH will persist. The decrease in pH at such critical sites will induce pitting corrosion [4]. Normally, the implant placed on the fractured bone is subjected to unbalanced weight-bearing biomechanical forces, resulting in bending and torsional stresses, and hence the implant may undergo a cyclic loading [3]. The propagation of stress corrosion and corrosion fatigue cracks and mechanical fatigue fracture can thus originate from the corrosion pits [4, 5]. The effect of a local decrease in pH on the stainless steel implant at the fractured bone site can be avoided by using nitrogen-bearing duplex stainless steel as an implant material, because the nitrogen released from this alloy at such critical sites can form ammonium ions by utilizing H^+ ions at such sites.

4. Conclusions

The following conclusions are obtained from the present investigations:

1. Super-ferritic stainless steel showed immunity to localized corrosion attack, even in the presence of crevices.
2. The pitting potential of duplex stainless steel was more noble than that of 316L stainless steel, implying that initiation of corrosion pits in this alloy was more energetically blocked in simulated body conditions.
3. The pit protection potential for duplex stainless steel was more noble than the corrosion potential. The repassivation of actively growing pits is considerably increased in this alloy.
4. Duplex stainless steel showed superior resistance to crevice corrosion due to the presence of nitrogen in this alloy. This is attributed to the formation of ammonium ions and ammonium nitrides at the pits present in the crevices, which slowed down the pit growth kinetics with an increase in the pH of the solution inside the pits.
5. The accelerated leaching study indicated very low leaching of metal ions from duplex and super-ferritic stainless steels, when compared with the commonly used 316L stainless steel.
6. The localized corrosion resistances of ferritic (Sea-cure) and duplex (SAF-2205) stainless steels in the simulated body environment were sufficiently high to prevent the onset of pitting and crevice corrosion.

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