Reviewed articles

Corrosion behaviour of Ti6Al4V and duplex stainless steel (UNS31803) in synthetic bio-fluids

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Keywords

Corrosion, Alloys, Steel, Medical products

Abstract

Compares the corrosion behaviour of Ti6Al4V titanium alloy, a conventional duplex stainless steel (UNS 31803) and AISI 304 austenitic stainless steel in synthetic biofluids using electrochemical techniques and comments on the suitability of DSS for use in biomedical applications. Finds that the general corrosion resistance of duplex stainless steels is slightly inferior to that of austenitic stainless steel and titanium alloy; duplex stainless steel does not show any sign of pitting when exposed to synthetic biofluids and exhibits excellent resistance to localised corrosion on par with that of titanium alloy. Concludes that duplex stainless steels are one of the best alternates to titanium alloys.

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Introduction

The use of metallic materials as surgical implants and prosthetic devices is well known for a long time (Williams, 1983; Williams and Meachim, 1974) and they are chosen because of their inherent mechanical properties. In general, the metals or alloys used for the application must be of highly corrosion resistant (Williams, 1983), biologically inert (Sury, 1977) and capable of being fabricated as an implant of suitable design at a reasonable cost. The most widely used implant materials are stainless steels (mostly austenitic grade), titanium alloys and cobalt based alloys (Bruneel and Helsen, 1988; Sivakumar *et al.*, 1993). The materials employed as orthopaedic devices in human body, classified as "prosthesis" and "implants", are exposed the living cells, tissues and biological fluids. The austenitic stainless steel of grade AISI 316L corresponding to the medical grade of ASTM F 138, though widely employed owing to the good general corrosion resistance and mechanical properties, suffer from the problem of localised corrosion, which causes leaching of metallic ions into the tissues surrounding the implants (Nielsen, 1987; Greene and Jones, 1966). The complicated service conditions (the human body fluids contain minerals, ionic salts, hydrolytic enzymes, proteins, nucleic acids, gases, carbonates and libids and hence highly harsh environment) and the high load encountered makes the material to fail. Stainless steels have generally been used as implant materials and titanium alloys are preferred to be employed as prosthetic devices, owing to their excellent general/localised corrosion resistance. However, due to the high cost factor and difficulties in machining, titanium and cobalt based alloys cannot always be regarded a competitive materials for these applications (Cigada *et al.*, 1989). Duplex stainless steels owing to their better mechanical properties, good formability/machinability and excellent corrosion resistance to both localised and stress corrosion cracking can be thought of as alternate material to the expensive titanium and cobalt alloys. The localised corrosion resistance of duplex stainless steels is due to the presence of alloying elements such as molybdenum and nitrogen. The pitting resistance of duplex stainless steels, which can normally be assessed by the pitting resistance

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equivalent number (PRE_N), is of the order of 32–40 as against 25–30 in the case of austenitic stainless steels. The higher pitting resistance in the case of DSS is attributed to the beneficial effect of nitrogen (Bernhardsson, 1991; Striecher, 1997).

The aim of the current work is to compare the corrosion behaviour of the highly attractive Ti6Al4V titanium alloy, a conventional duplex stainless steel (UNS 31803) and AISI 304 austenitic stainless steel in synthetic biofluids using electrochemical techniques and comment on the suitability of DSS for use in biomedical applications.

Experimental

The materials employed in this investigation were (a) Ti-6Al-4V titanium alloy and (b) duplex stainless steel—DSS (UNS 31803), with a chemical composition 0.02 percent C, 22 percent Cr, 5 percent Ni, 3 percent Mo and 0.15 percent N and (c) an austenitic stainless steel—ASS (AISI 304). Specimens of size 40×25 × 5 mm have been prepared from the respective materials and the corrosion studies were made on the samples prepared to the metallographic finish.

The metallographic observations were made in a Jenavert microscope and representative regions from each sample have been photographed under bright field illumination. The specimens used for metallographic observation were subjected to hardness testing in a Zwick hardness testing machine under a load of 50N.

Potentiodynamic polarisation and impedance studies have been made in 1 percent NaCl, Hank's and Cigada solutions. The test solution compositions were as given in Table I. A three-electrode cell was employed for the studies, with specimen, platinum and a calomel being used as working, auxiliary and reference electrodes respectively. Analar grade chemicals and double distilled water were employed for making test solutions. Potentiodynamic polarisation studies were performed at a scan rate of $0.5\,mV\,s^{-1}$ in non-deaerated test solution.

Results and discussion

Figure 1(a) and (b) show the optical micrograph of duplex stainless steel and Ti6Al4V. As can be seen, the duplex stainless steel has a two-phase structure, with equal amounts of austenite and ferrite. In the case of titanium alloy also a two-phase structure could be noticed, the α and β phases being revealed as dark and light etched regions. The hardness values of duplex stainless steel and titanium alloy are 250 VHN and 335 VHN respectively. In this condition, the machinability of DSS was found to be comparable to that of the conventional austenitic stainless steels, whereas the titanium alloy was difficult to be machined with conventional tooling.

Typical potentiodynamic polarisation curves obtained for duplex stainless steel (DSS), austenitic stainless steel (ASS) and Ti6Al4V in the synthetic bio-fluids are shown in Figures 2–4 respectively. The electrochemical parameters have been summarised in Tables II–IV.

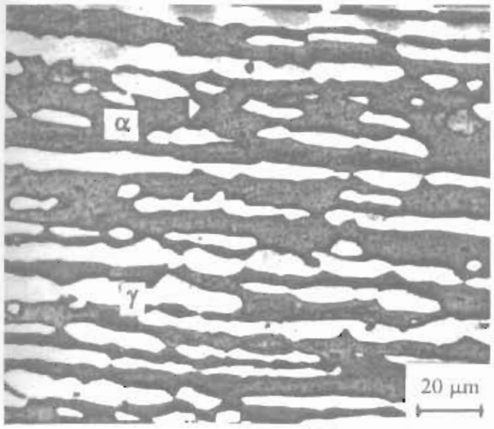
From the tables, it is clear that the corrosion potential of DSS is more active and the corrosion current (in the order of 0.4–0.5 $\mu A\,cm^{-2}$) is higher than that of the

Table I Composition of test solutions ($g\,l^{-1}$)

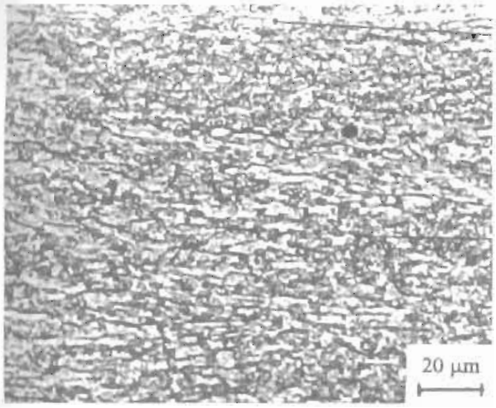
Compound ($g\,l^{-1}$)	1 percent NaCl	Hank's Solution	Cigada Solution
NaCl	10.00	8.00	8.75
$CaCl_2$	–	0.14	–
KCl	–	0.40	–
$NaHCO_3$	–	0.35	0.35
Glucose	–	1.00	–
NaH_2PO_4	–	0.10	0.06
$MgCl_2.6H_2O$	–	0.10	–
$Na_2HPO_4.2H_2O$	–	0.06	0.06
$MgSO_4.7H_2O$	–	0.06	–

Test temperature: ambient; pH of solution: 7.2–7.4

Figure 1 Optical micrograph of (a) duplex stainless steel and (b) titanium alloy Ti6A14V



(a) Optical micrograph of duplex stainless steel



(b) Optical micrograph of titanium alloy Ti6A14V

austenitic stainless steel (0.05–0.2 μA cm^{-2}) and titanium alloy. The plausible reason for the higher corrosion current is the preferential dissolution influenced by the galvanic coupling between the two phases when DSS is exposed to the electrolyte. Depending upon the solution composition, the result is either an accelerated preferential attack of the ferrite phase, or, in solutions where austenite has a substantially lower corrosion resistance than ferrite, a satisfactory protection of the austenite phase and a more uniform corrosion rate over the whole surface (Symniotis, 1990; Symniotis, 1995). It becomes clear that active corrosion of DSS often results in an uneven distribution of the attack over the surface.

Current oscillations have been observed near the passive/passive-to-breakdown potentials and it is more in 1 percent chloride solution. The oscillations can be attributed to the presence of surface inhomogeneities and the chloride ions. A minimum concentration of chloride in the solution is necessary for fluctuations. A qualitative explanation for this phenomenon was given by Podesta *et al.*, for the current oscillations of stainless steel (Podestaaa *et al.*, 1982). It is interesting to note that both the DSS and Ti6Al4V alloy exhibit a wider passive regions in these bio-fluids, whereas, the austenitic stainless steel show a very narrow passive regions only.

In 1 percent chloride solution, the ASS shows passivation for a very narrow range (100 mV) with a passivation current in the order of 10^{-7} A cm^{-2}. The DSS passivates to a wide range (1,300 mV) and for the Ti6Al4V the range is still wider, with passivation current in the order of 10^{-7}–10^{-5} A cm^{-2}. In Hank's and Cigada solutions, also a similar behaviour was observed.

Pitting is a form of localised attack on the implant due the breakdown of passivity. Pitting corrosion occurs frequently in media containing higher chloride ions (Man and

Figure 2 Potentiodynamic polarisation behaviour of Ti6A14V, duplex stainless steel and austenitic stainless steel in 1 percent NaCl solution

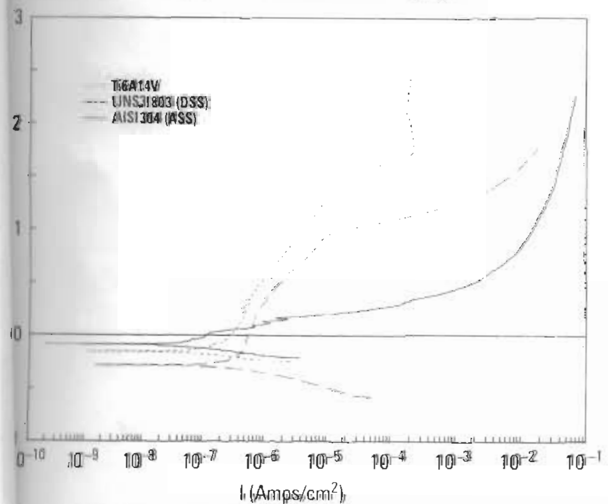


Figure 3 Potentiodynamic polarisation behaviour of Ti6A14V, duplex stainless steel and austenitic stainless steel in Cigada solution

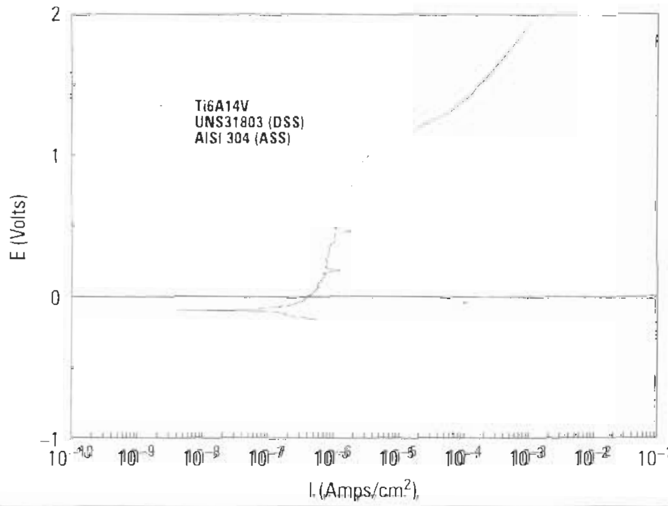


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Table II Electrochemical data for implant materials in 1 percent NaCl so,lution

Material	E_{corr}, *mV (SCE)*	I_{corr}, *µA cm^{-2}*	I_{pass}, *µA cm^{-2}*	Passive range, mV(SCE)	E_{pit}, *mV (SCE)*
ASS	− 75	0.05	0.1−0.4	100	+20
DSS	− 300	0.40	0.4−10.0	1350	+1050
Ti6Al4V	− 135	0.10	0.1−10.0	Very wide	No breakdown

Table III Electrochemical data for implant materials in Cigada solution

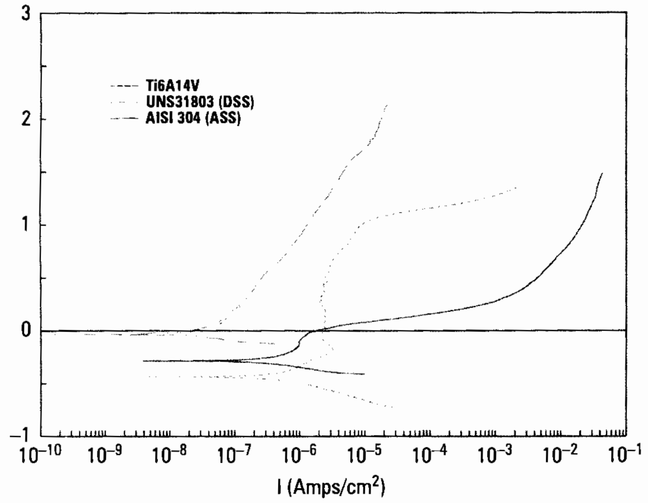
Material	E_{corr}, *mV (SCE)*	I_{corr}, *µA cm^{-2}*	I_{pass}, *µA cm^{-2}*	Passive range, mV(SCE)	E_{pit}, *mV (SCE)*
ASS	− 300	0.06	0.07−0.2	250	0
DSS	− 400	0.50	0.8−5.0	1450	1060
Ti6Al4V	− 130	0.40	0.4−2.0	Very wide	No breakdown

Table IV Electrochemical data for implant materials in Hank's solution

Material	E_{corr}, *mV (SCE)*	I_{corr}, *µA cm^{-2}*	I_{pass}, *µA cm^{-2}*	Passive range, mV(SCE)	E_{pit}, *mV (SCE)*
ASS	− 250	0.20	0.8−1.0	200	0
DSS	− 420	0.40	2.0−7.0	1400	1020
Ti6Al4V	− 30	0.04	0.04−10.0	Very wide	No breakdown

Gabe, 1981). It has been reported that the pits on the implants can act as nucleation sites for the fatigue and stress corrosion cracking (Sivakumar *et al.*, 1992). The presence of increased oxygen and chloride content in the body fluid, and the presence of ionic salts, are reported to act as pitting agents for the implant material. In this investigation, the value of the potential at which the anodic current increased abruptly was taken as pitting potential, E_{pit}. Three test runs were carried out for each sample in each of the bio-fluids and the average of results are reported. The value of E_{pit} was found to vary with in ± 15 mV for the same sample in each electrolyte.

Figure 4 Potentiodynamic polarisation behaviour of Ti6A14V, duplex stainless steel and austenitic stainless steel in Hank's solution



From Table II, it is evident that even though the DSS has inferior general corrosion resistance, the pitting resistance is much higher than the ASS, and is comparable to that of the Ti6Al4V alloy. The higher resistance offered by the DSS in these bio-fluids is due to the distribution of alloying elements as reported based on electron probe microanalysis study (Charles, 1991). The study of the DSS showed enrichment of Cr and Mo in ferrite phase and nitrogen in the austenite. The PRE_N values for the ferrite and austenite were quite similar. The high pitting resistance seems to arise from synergism between molybdenum and nitrogen or lower levels of residual elements such as phosphorous(Charles, 1991).

Duplex stainless steels samples were exposed to Cigada and Hank's solution for a period of 10 days at room temperature. Another sample was exposed to the same electrolyte with current impressed to shift the potential into the passivation range (potential fixed at 400 mV vs. SCE). The test solutions were analysed for leaching of alloying elements, especially the highly toxic nickel. The analysis did reveal that the dissolution rates are extremely low in both the cases and no trace of nickel could be detected even by the qualitative analysis using dimethyl glyoxime. The above observations clearly demonstrated the high degree of suitability of duplex stainless steels for use as implant materials if not as prosthesis devices.

Conclusions

- The general corrosion resistance of duplex stainless steels in synthetic biofluids is found to be slightly inferior to that of austenitic stainless steel and titanium alloy.
- The duplex stainless steel does not show any sign of pitting when exposed to synthetic biofluids and exhibited an excellent resistance to localised corrosion on par with that of titanium alloy.
- From the dissolution studies on DSS conducted in Hank's and Cigada test solutions, it can be concluded that the duplex stainless steels are one of the best alternates to titanium alloys, keeping in view the high cost factor.

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