4. The Effect of Shape and Surface Modification on the Corrosion of Biomedical Nitinol Alloy Wires Exposed to Saline Solution

4.1 Introduction

The Corrosion behaviour of Nitinol wire that has been chemically etched and mechanically polished was studied in a corrosive 0.9% Saline solution. The electrochemical corrosion tests conducted on the as-received straight and curved wires of nitinol included open circuit potential measurement, polarisation resistance and Tafel plots. The chemically etched looped wires exhibited the highest recorded corrosion potential Ecorr and the lowest values of corrosion current icorr. The results of the open circuit potential (OCP) measurements and polarisation resistance, combined with scanning electron microscopy (SEM) indicated the presence of a protective passive corrosion resistant film on the chemically etched wires.

One of the most popular shape-memory and super-elastic alloys used for biomedical stents is called Nitinol. It exhibits a number of favourable material properties that makes it well suited for use as a stent [1]. Its most important properties are the super elasticity and shape memory abilities. Nitinol's ability to be deformed by more than 10% strain and elastically recover its original shape is described as super elasticity. The material is able to withstand a stress, which induces an elastic deformation, thus causing the material to undergo a phase transformation. Superelasticity results from a stress-induced transformation while shape memory results from a thermal phase transformation. Both of these properties are employed in Nitinol stents [2].

Biocompatibility is always an issue whenever implanting a foreign material into the human body [3]. Implanting metals brings its own set of problems, such as corrosion.

When a metal is introduced into the body, a wide variety of processes and interactions with the biological environment can take place. Such processes include metal ion release [4]; oxide formation, either as a apassive oxide film [5] or as a particulate oxide; and corresponding reduction reactions that typically involve oxygen reduction but may also include biochemical species such as proteins [6]. These phenomena vary microscopically over the alloy surface and depend on the local environment, local alloy composition and structure as well as local mechanical factors [7].

The aim of the current investigation is to study the corrosion and pitting resistance behaviour of nitinol wire with different surface finishes i.e. chemical etching and mechanical polishing. The corrosion test was conducted in 0.9% saline solution at 37°C by means of electrochemical measurements. OCP, pitting potentials, corrosion potentials and corrosion currents were analysed in each of the materials studied.

4.2 Experimental Methods

The materials under investigation were Nitinol wire that had been mechanically polished with a diameter of 0.2mm and nitinol wire that had been chemically etched with a diameter of 0.2mm provided by Vascutek of Renfrewshire, Scotland, U.K. The material compositions are shown in Table 4.1, from EDX analysis.

The solution used was a commercial NaCl solution, from Parkfields Pharmaceutical limited which contains sodium chloride B.P. 0.9% w/v in purified water B.P. The experimental arrangement used consists of the electrochemical unit including the Voltalab 40 (PGZ301) potentiostat that is able to perform conventional electrochemical measurements dedicated to corrosion techniques. The overall system was controlled using a PC-compatible microcomputer with Voltamaster 4 electrochemical software and a basic corrosion cell whose body is made of pyrex with a double jacketed device allowing thermostatic experiments to be performed (ISO 10993-15).

The experiments were carried out at 37 +/– °C by circulating the water through the double wall of the cell. The working electrode with a surface area of about 1cm^2 was inserted into the cell through a rubber sealer. The apparatus and the electrochemical cell conformed

Table 4.1. Materials composition: (e) Elemental percentage, (a) Atomic weight percentage

Material	Ni(e)	Ti(e)	Total(e)	Ni(a)	Ti(a)	Total(a)
Mechanical Polished	54.4	45.5	100.0	49.5	50.5	100.0
Chemical Etched	53.8	46.2	100.0	48.8	51.2	100.0

to ATM G5-94. The potential of the working electrode was measured against the reference calomel electrode, which contained a porous pin liquid junction and a saturated KCl salt bridge solution from Radiometer analytical. A platinum wire metal electrode was used as the auxiliary counter electrode. The electrolyte was continuously purged with purified nitrogen gas to de-aerate the solution for 1hr before OCP and polarization experiments.

4.2.1 Electrochemical Testing Procedure

OCP and potentiodynamic anodic polarization measurements were conducted according to ASTM G5 test generated using a potentiostat. The OCP was determined after 22hr for 0.9% saline solution, the value obtained after stabilisation of the curve being called the rest potential. Potentiodynamic anodic polarization test was scanned at −1000mV to 2500mV at a scan rate of 0.167 mV/sec in order to determine corrosion and breakdown potentials. Current corrosion density (*i*corr), corrosion potential (Ecorr) and breakdown potential (E$_{bp}$) were obtained from polarization curves using the Tafel slopes.

4.2.2 Experimental Results

Open Circuit Potential (OCP)

OCP is the thermodynamic measurement of how likely the surfaces are to corrode. The more positive an OCP the more stable is the oxide film on the surface and therefore the less reactive the surface. The OCP was measured to determine the stable corrosion potential (Ecorr) of the nitinol alloy samples, i.e., the values obtained when the potential becomes constant (Fig. 4.1).
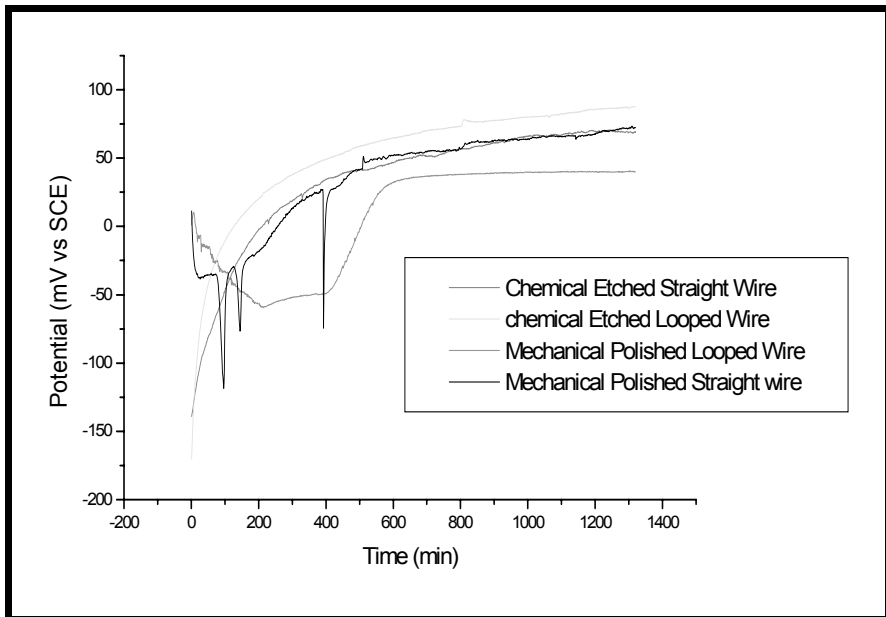
Fig. 4.1. OCP vs. time curves for the stable potential determination of nitinol in 0.9% saline solution

The OCP value for chemical etched wire in looped geometry proved to be the most positive value of OCP, the wire progressively becomes more anodic with time, the oxide layer film remains intact and the material stays stable in the passive state, and is therefore the least reactive surface in 0.9% saline. The Mechanically polished wire initially shifted towards more negative values before stabilising in more positive values after 22hrs. Table 4.2 shows the OCP values table of the nitinol wires after 22hrs.

Tafel Plot

Tafel plots of the different surface treatments Fig. 4.2 are used to measure the corrosion current i_{corr}, which is then used to calculate the corrosion rate. The Tafel plot yields the Tafel constants β_A and β_C which is used with polarisation resistance (Rp) [8,9] data to calculate corrosion rate as shown in Table 4.3. Results show chemical etched looped sample with the highest corrosion potential and the chemical etched straight wire with the lowest corrosion potential. The results

Table 4.2. OCP values after 22hrs in 0.9% saline

Sample	OCP (mV)
Chemical Etched	67
Mechanical Polished	32
Chemical Etched Looped	87
Mechanical Polished Looped	40

indicate that the chemically etched looped wire is the most stable of the wires, with the highest corrosion potential, a low corrosion current and low corrosion rate as shown in Fig. 4.3.

Potentiodynamic Curves

The potentiodynamic curves are as shown in Fig. 4.4. The potentiodynamic curves indicate the passivation tendencies of the wires, in the passive region. Results from Fig. 4.4 show that the chemically etched looped wire has the largest passivation region, i.e., (–0.78mV to +448mV) [9].

The breakdown potentials (E_{bd}) correspond to the breakdown of the passive surface film, which is identified by the sudden increase in the current flowing in the solution, as shown in Table 4.4.

Table 4.3. Tafel parameters for NiTi wires in 0.9% saline solution

Sample	E_{corr} (mV/)	i_{corr} ($\mu A/cm^2$)	βA (mV/)	βC (mV/)	Rp (mV/)	CR ($\mu m/yr$)
Chemical Etched	–317.8	0.14	68.8	–162.0	0.13	3.74
Mechanical Polished	–235.6	0.13	116	–69.6	0.14	3.60
Chemical Etched Looped	–164	0.18	97.4	–75.5	0.10	4.89
Mechanical Polished Looped	–175	0.11	72.8	–56.9	0.12	3.07

Table 4.4. Breakdown potential of the nitinol wires in 0.9% saline

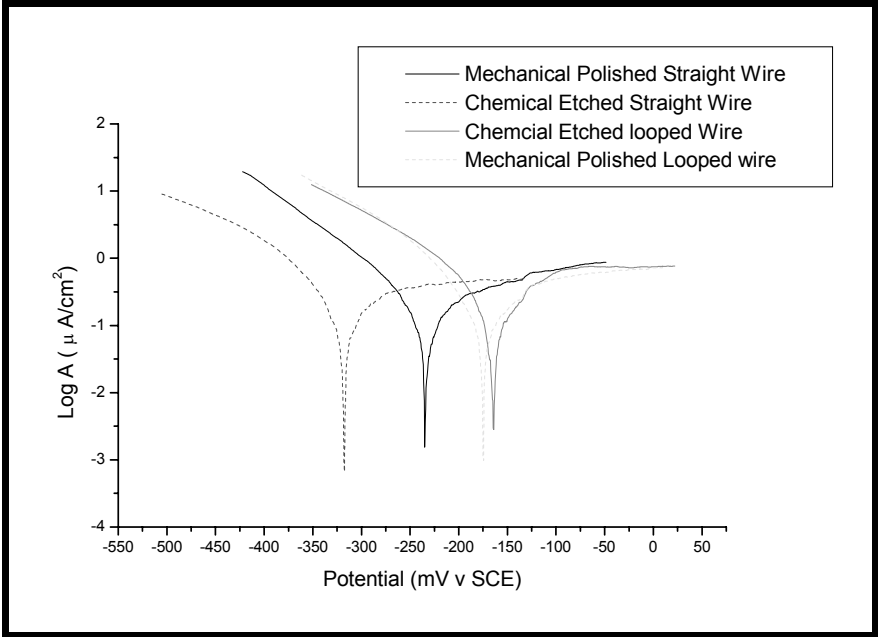| Sample	E_{corr} (mV/)	E_{brk} (mV/)	i_{brk} ($\mu A/cm^2$)
Chemical Etched	–317.8	331	0.66
Mechanical Polished	–235.6	248	0.8
Chemical Etched Looped	–164	445	1.2
Mechanical Polished Looped	–175	172	0.81

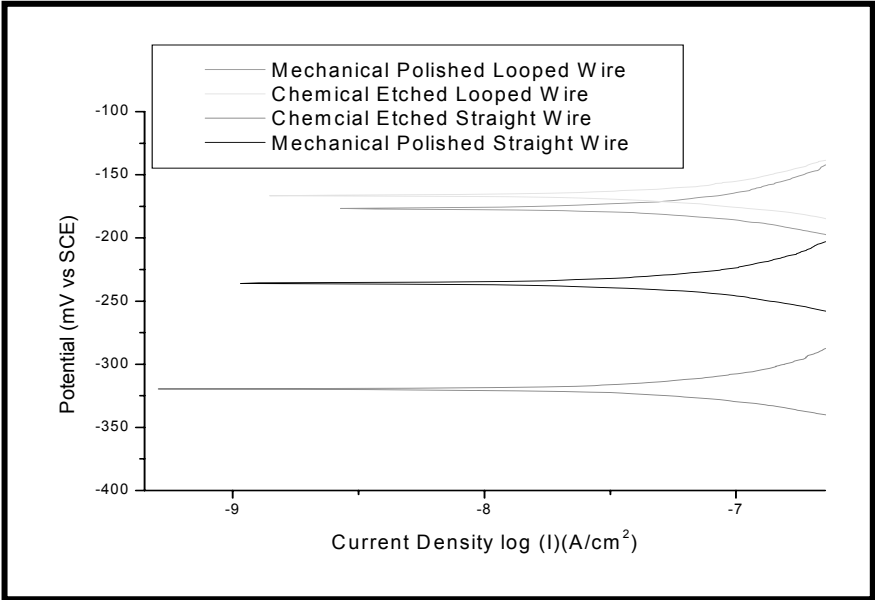**Fig. 4.2.** Tafel plot of wires in 0.9% Saline solution

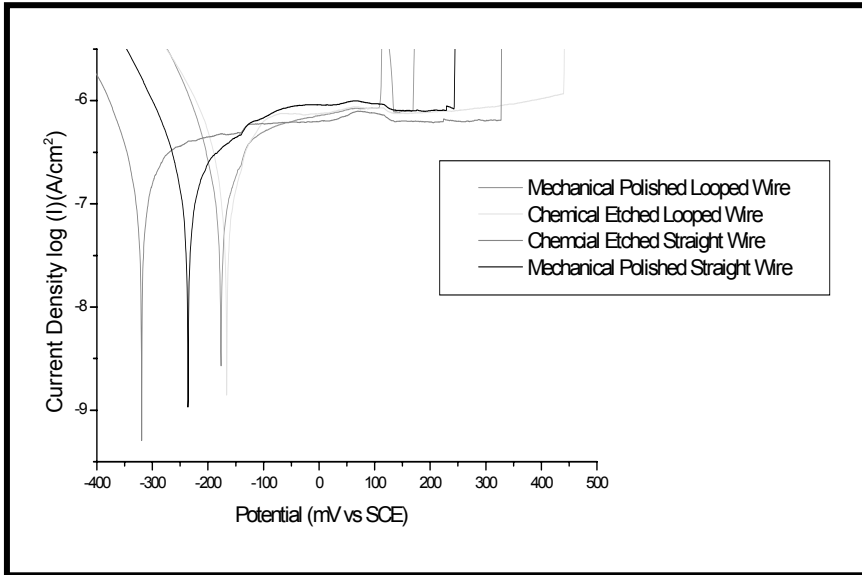**Fig. 4.3.** Tafel curve looking at Ecorr and icorr saline solution

Fig. 4.4. Passivation region of potentiodynamic curve in 0.9% saline
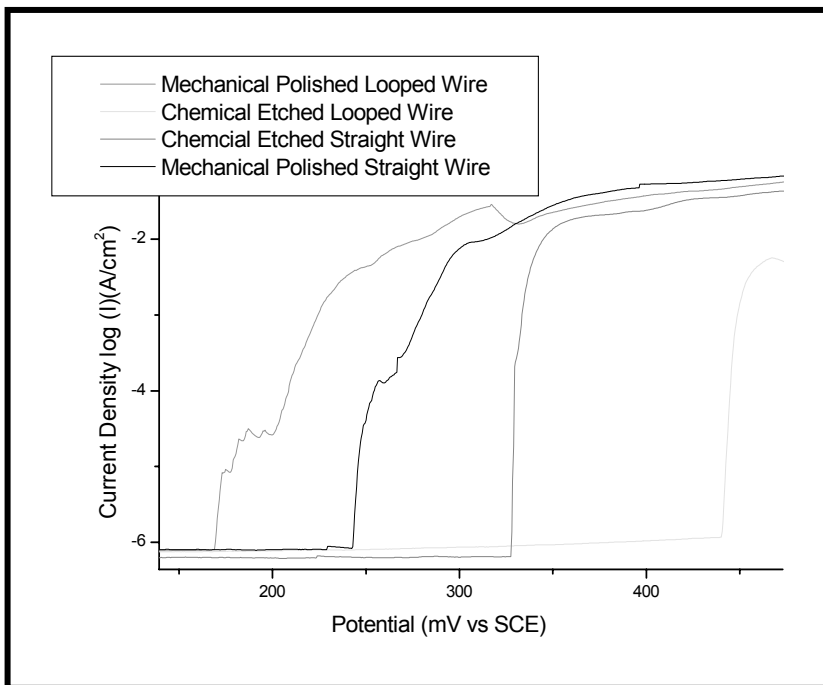

Fig. 4.5. Corrosive region (transpassive region) of the potentiodynamic curve in 0.9% saline

Fig. 4.5 shows the corrosive region of the different wires from the potentiodynamic curve, where there is a sudden increase in the current.

Anodic Polarisation (Localised Pitting Test)

Anodic polarisation behaviour of passive metals examines pitting and crevice corrosion susceptibility. Pitting corrosion occurs when the oxide passive film layer breaks down locally. After local break-down of the film an anode forms where the film has broken down whilst the unbroken film acts as the cathode. This then accelerates localised attack and pits develop at the unbroken spots. The "pitting potential" corresponds to the potential at which the current starts to increase on the anodic scan. The "repassivation potential" corresponds to the potential at which the current becomes negligible on the reverse (cathodic) scan. A "repassivation potential" close to the "pitting potential" indicates that the sample is capable of re-protecting itself easily after pitting. Figures 4.6–4.7 are graphs of anodic polarisation. From these curves it is possible to determine how prone to pitting a metal is in a particular environment.
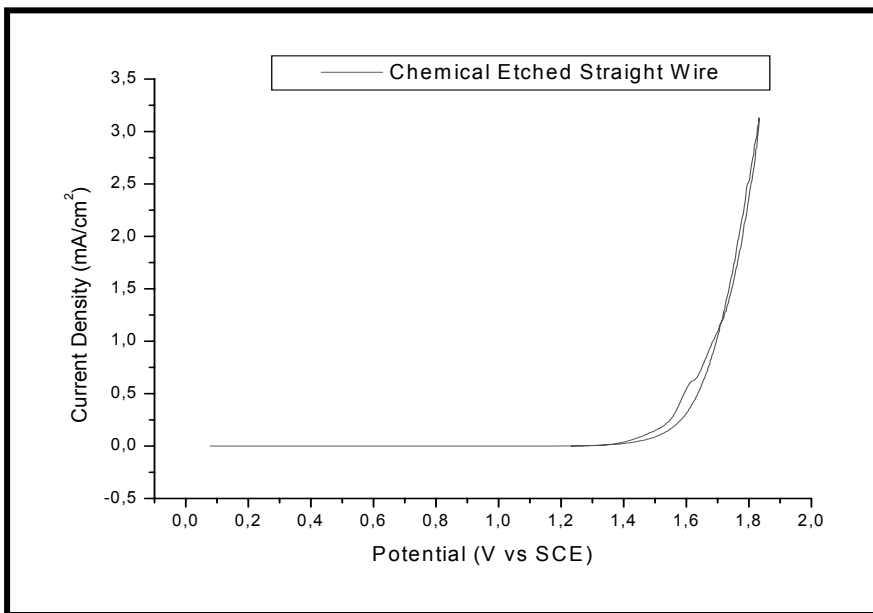

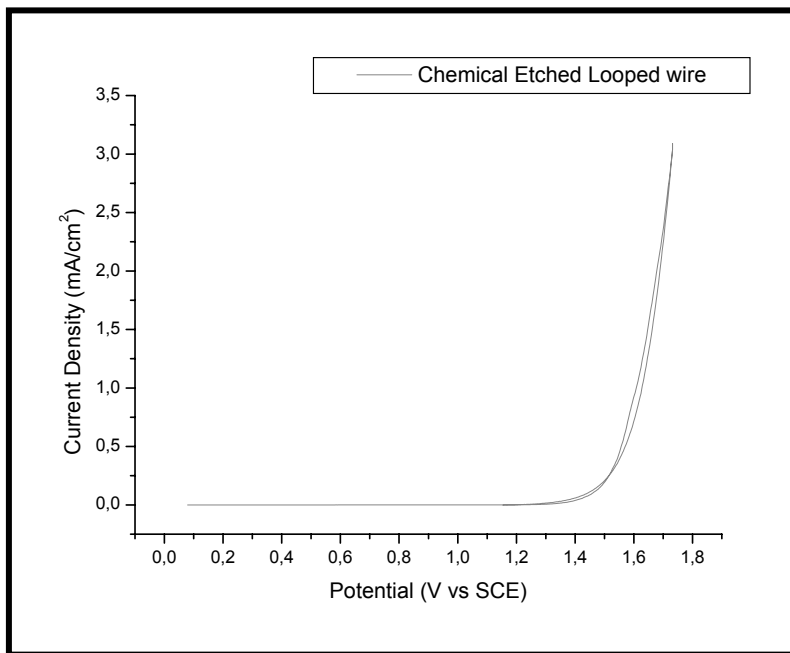**Fig. 4.6.** Anodic polarisation of chemical etched straight wire in 0.9% saline

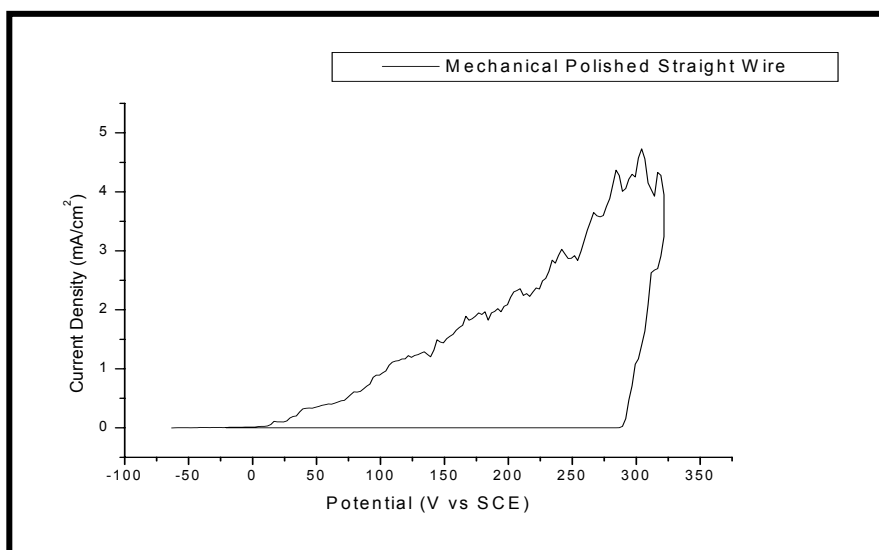**Fig. 4.7.** Anodic polarisation of chemically etched looped wire in saline solution

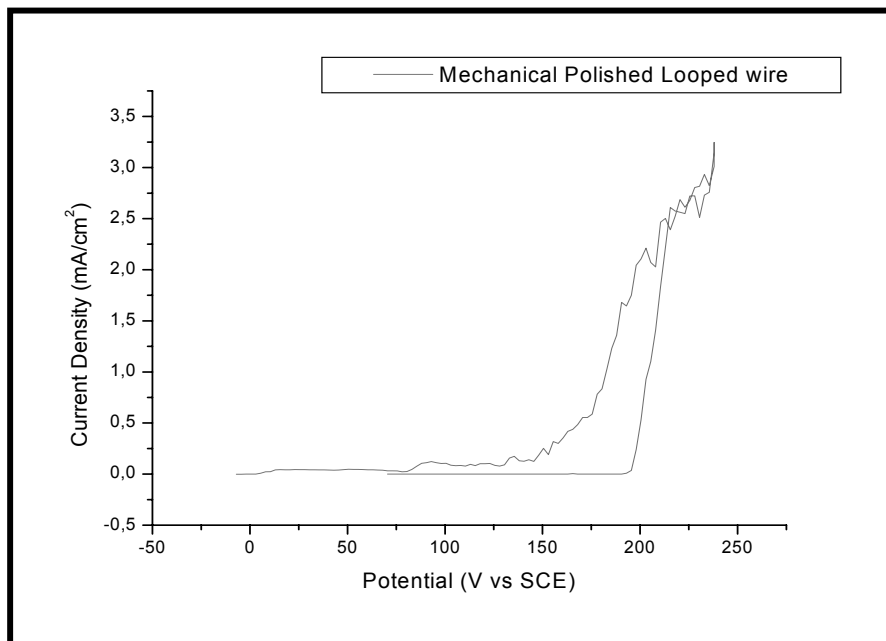**Fig. 4.8.** Anodic polarisation of mechanically polished straight wire in 0.9% saline

Fig. 4.9. Mechanically polished looped wire in Saline solution

Anodic polarisation curves reveal the pitting corrosion potential of the chemical etched straight wire at 1415mV and the chemical etched looped wire at 1451mV as shown in Figs. 4.6–4.7 whilst the pitting in the mechanically polished straight wire is at 289mV and the mechanical polished looped wire is at 233mV as shown in Figs. 4.8–4.9. The protection potential also known as the repassivation potential is the potential at which the current becomes negligible on the reverse scan. For the mechanical polished wire the repassivation potential is observed at 13.3mV, whilst the repassivation for the chemical etched wire is observed to 1382mV. The mechanical polished surfaces undergo early pitting below 300mV as shown in Figs. 4.8–4.9 whilst the chemical etched surfaces remain stable for a while before pitting takes place above 1400mV as shown in Figs. 4.6–4.7. Results also show pitting potential (Epitt) and repassivation potentials (Erep) are rather close for the chemically etched surface samples. For the mechanically polished surfaces the Epitt and Erep potentials are very far apart. Pitting potential and protection potential calculated from the pitting corrosion curves are shown in Table 4.5.

Table 4.5. Pitting potential and repassivation potential of material in 0.9% saline

Sample	E_{Pitt} (mV)	E_{rep} (mV)	E_{Pitt}- E_{rep} (mV)
Chemical Etched	1415	1382	33
Mechanical Polished	289	13.3	275
Chemical Etched Looped	1451	1451	42
Mechanical Polished Looped	233	200	33

A repassivation potential close to the pitting potential indicates that the sample is capable of re-protecting itself easily after pitting.

Surface Studies

SEM images of chemical etched and mechanical polished wires before and after corrosion in 0.9% saline are as shown in Fig. 4.10 (a-f)

The SEM images in Figs. 4.10b-c show the chemical etched wire after the pitting test. It is evident that no pitting or corrosion took place. The surface of the wire is not as smooth as the as-received wire. There was no significant difference between the looped and the straight geometry. Both pitting and corrosion would seem to have taken place on the surface of the mechanically polished wires in Figs. 4.10e-f. The mechanically polished looped wire in Fig. 4.10f appears to have undergone excessive pitting. In certain areas on the
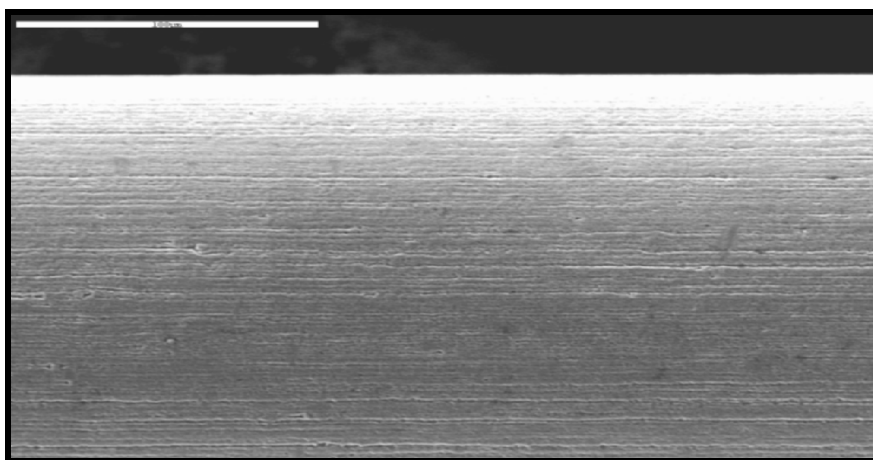

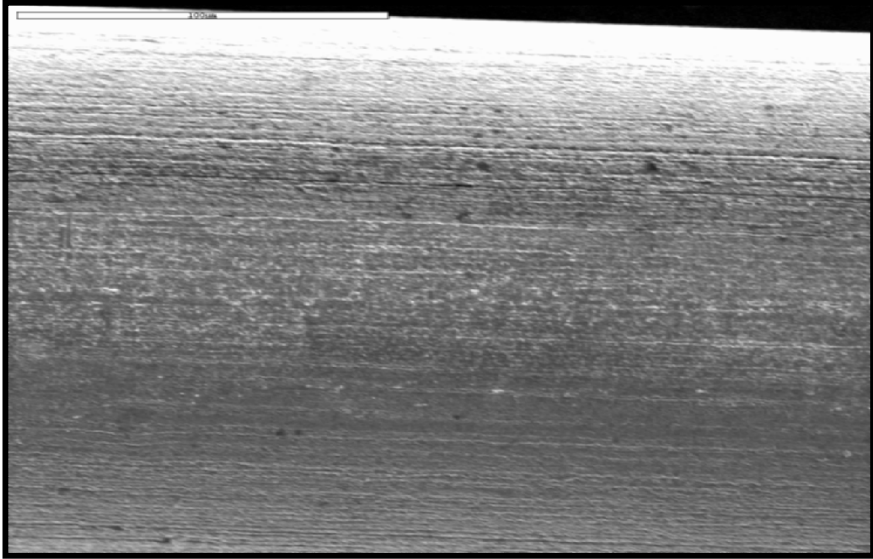**Fig. 4.10a.** SEM image of chemical etched surface before corrosion (scale bar 100μm)

Fig. 4.10b. SEM image of chemically etched straight surface after the potentio-dynamic test (Magnification x500)
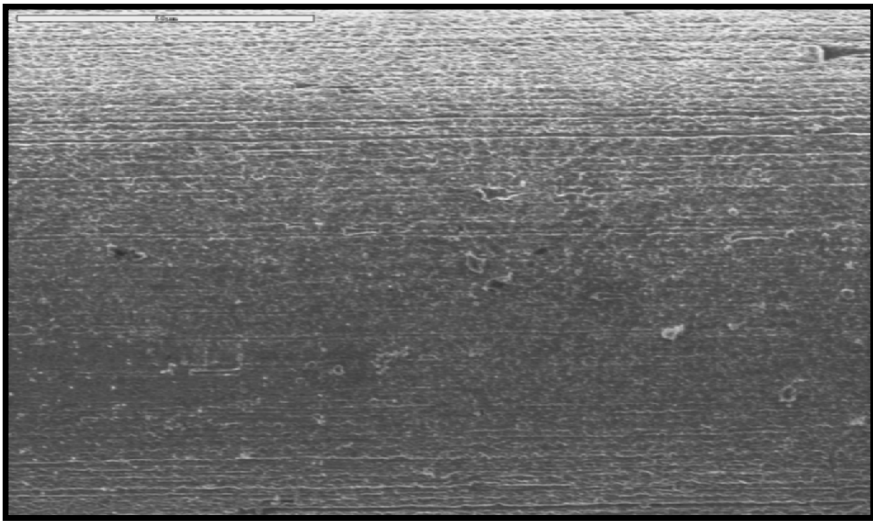

Fig. 4.10c. SEM image of chemically etched looped surface after potentiodynamic test (Magnification x500)
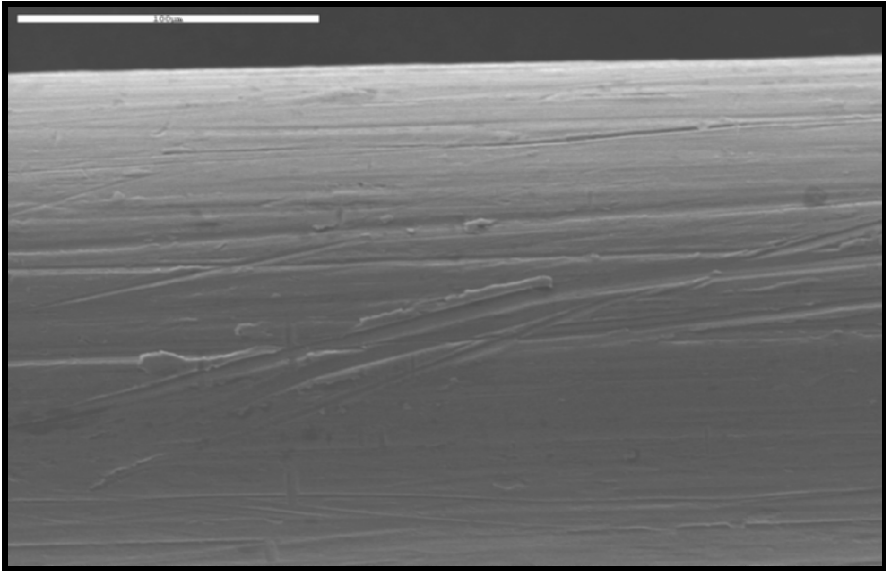
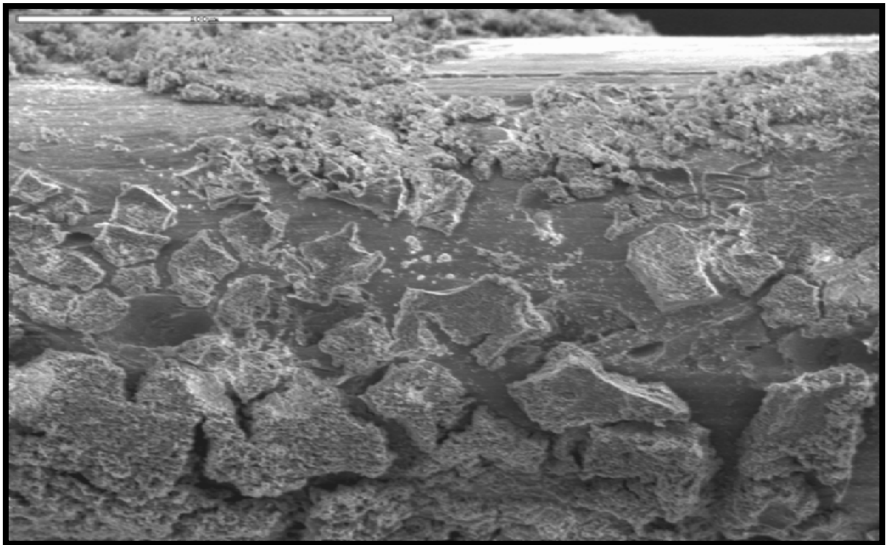**Fig. 4.10d.** SEM image of mechanically polished wire before corrosion (scale bar 100μm)

Fig. 4.10e. SEM image Mechanically Polished Straight wire after potentiodynamic test (+3500mv) (scale bar magnification x500)
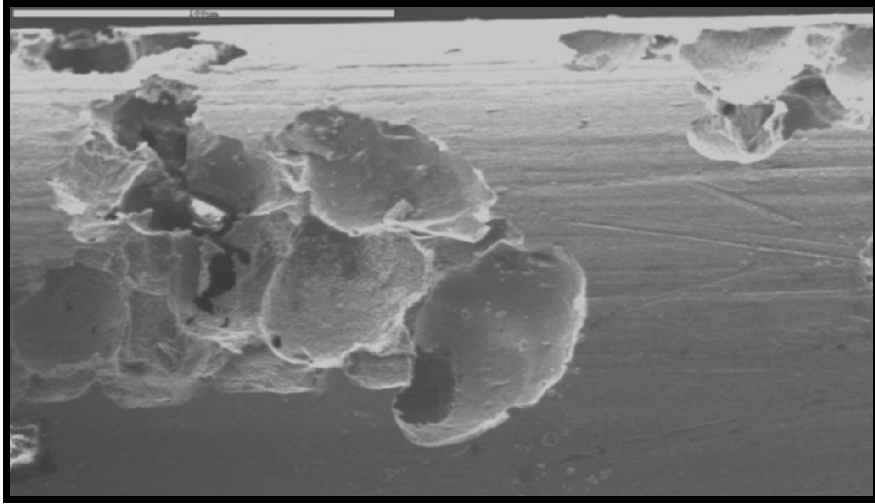
Fig. 4.10f. SEM image Mechanically Polished looped wire after potentiodynamic test (+3500mv) (scale bar magnification x500)

surface the pits have turned into cracks. Pitting is only observed on certain areas of the surface and other areas have been left untouched. The crumbling effect of the oxide layer on the mechanically polished straight wire can be observed in Fig. 4.10e. Also it appears that the oxide layer has been broken into smaller parts so that another layer on the mechanical polished wire can be observed. EDX analysis of the chemical etched wire after potentiodynamic test of +3500mV. Fig. 4.11a showed reduced nickel content of less than 10cps on the surface; whilst nickel content of the mechanical polished wire had remained the same at around 70cps as shown in Fig 4.11b.

4.3 Summary

The effect of a saline corrosive environment on a typical composition of nitinol alloy used as an implant material in the human body has been investigated. The investigation considered the effect of two surface treatments, namely, mechanical polishing and chemical etching using a proprietary technique, on the resistance of nitinol wires to a corrosive saline environment. It is also considered that the effect of
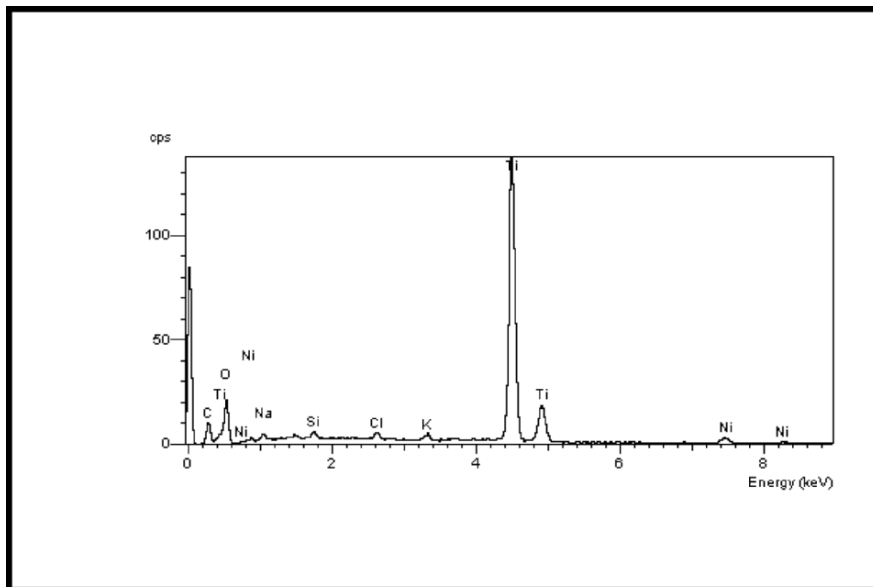
Fig. 4.11a. EDX analysis of chemically etched wire PD +3500mV having very little nickel on its surface
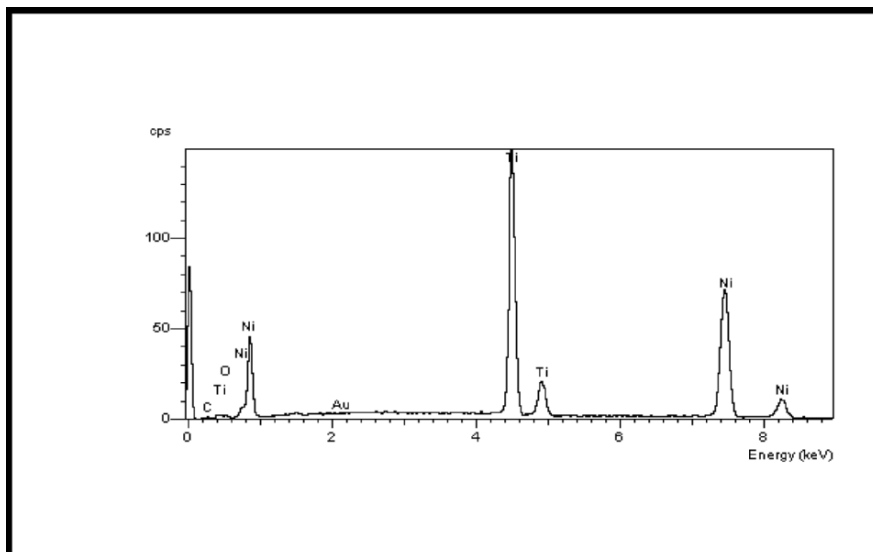

Fig. 4.11b. EDX analysis of mechanically polished wire PD +3500mV

an imposed geometry may change the corrosion that the effect of an imposed geometry may change the corrosion conditions, i.e., whether the wires are exposed to the saline solution as straight or looped wires on their resistance to corrosion in a saline environment. It is observed the most positive open circuit potential (OCP) after 22 hours on the chemically etched wire. Tafel plot results also indicated that the chemically etched looped wire had the largest passive region and the re-passivation and pitting potentials were found to be quite close to each other for the chemically polished wire. There was a more substantial difference between the re-passivation and the pitting potential of the mechanically polished nitinol wires, indicating a higher susceptibility to pitting corrosion. This was confirmed by scanning electron microscopy (SEM) that showed substantial pitting on the mechanically polished wire, whilst the chemically etched wire appears to be almost unaffected by the electrochemical test in saline solution. The proprietary chemical treatment on the nitinol wire seems to be necessary for corrosion protection in applications where nitinol wire will be exposed to a corrosive saline environment.

Acknowledgements

References

1. Wu S. K., Lin H. C., Recent development of TiNi-based shape memory alloys in Taiwan, Mat. Chem & Phys., 2000: 81-92.
2. Stoeckel. D. P. A., Duerig. T., Self-expanding nitinol stent: material and design considerations, Eur Radiol 2004, **14**, 292-301.
3. Williams D. F., Fundamental aspects of biocompatibility, 1981, CRC Press: Boca Raton, Florida.
4. Cisse O., Savadogo O., Wu M., Yahia L. H., Effect of surface treatment of NiTi alloy on its corrosion behavior in Hanks' solution, Journal of Biomedical Materials Research, 2002, 339-345.
5. O'Brien B., Carroll W. M., Kelly M. J., Passivation of nitinol wire for vascular implants - a demonstration of the benefits, Biomaterials, 2002, 1739-1748.

6. Khan M. A., Williams R. L., Williams D. F., The corrosion behaviour of Ti-6Al-4V, Ti-6Al-7Nb and Ti-13Nb-13Zr in protein solution, Biomaterials 1999, 631-637.

7. Shabalovskaya S. A., Anderegg J., Laab F., Thiel P. A., Rondelli G., Surface conditions of nitinol wires, tubing and as-cast alloys: the effect of chemical etching, aging in boiling water and heat treatment., J. Biomed. Mat. Res., 2003, 339-345.

8. Ademosu O., Ogwu A. A., McLean J., Corrigan M., Placido F., Electro-chemical corrosion of chemically etched and mechanically polished nitinol wires in Hanks' and saline solution, International Conference on Surfaces, Coatings and Nanostructured Materials, nanoSMat2005, 2005a. Aveiro, Portugal.

9. Ademosu O., Ogwu A. A., Placido F., McLean J., Ashton T., Surface char-acterisation of modified biocompatible nitinol alloy wires exposed to saline and Hanks' physiological solution, Institute of Physics (UK) conference on Novel Applications of surface modification. 2005b., Chester College, UK.

10. Ernest B. Yeager, Center for Electrochemical Sciences (YCES) and the Chemical Engineering Department, Case Western Reserve University, Cleveland, Ohio. http://electrochem.cwru.edu/ed/encycl/art-c02-corrosion.htm#passiv. 2004.