JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE **16** (2005) 107–117

The influence of passivation and electropolishing on the performance of medical grade stainless steels in static and fatigue loading

L. M. WELDON[1], P. E. MCHUGH[1,3]*, W. CARROLL[2,3], E. COSTELLO[2], C. O'BRADAIGH[1]
[1]*Department of Mechanical and Biomedical Engineering and* [2]*Department of Chemistry, National University of Ireland, Galway, Ireland*
E-mail: peter.mchugh@nuigalway.ie
[3]*National Centre for Biomedical Engineering Science, National University of Ireland, Galway, Ireland*

The effects of surface passivation and electropolishing on the mechanical performance of a group of biomedical grade stainless steels have been investigated. Surface roughness measurements showed that the treatments had a significant effect on the final surface finish. However, static mechanical testing demonstrated no difference in static mechanical properties, regardless of surface treatment. High cycle fatigue testing was carried out at a frequency of 120 Hz with a load ratio of $R = 0.1$, in both air and a simulated *in vivo* wet corrosive environment. 316LVM (cold worked) proved superior to 316L (annealed) in fatigue performance, in both dry and wet environments. The fatigue performance of both materials did depend on the surface treatment, with electropolishing resulting in better performance than passivation. The fatigue performance of both materials was significantly better in the dry environment in comparison to the wet environment. The dry-to-wet deterioration in fatigue performance was somewhat dependent on the surface treatment for the 316L material but almost independent of surface treatment for the 316LVM material. Significant surface pitting and damage was evident for 316L during fatigue in the wet environment, whereas almost no pitting and damage was observed for 316LVM.

1. Introduction

Stainless steels of the 316L type are the most commonly used materials for coronary stents. Stents are thin-wire scaffold structures used in angioplasty for the treatment of atherosclerosis, and are permanently implanted into the body. Stainless steel stents are normally inserted on the tip of a balloon catheter, in an unexpanded or crimped state. At the desired location they are deployed (or expanded) to fit the artery diameter by the inflation of the balloon and remain expanded due to the plastic deformation of the metal.

The magnitude of the plastic deformation during deployment can be considerable [1] and hence the static mechanical properties and ductility of the material are important considerations in stent design. The fatigue properties of the stent material are also important since the stent will be subjected to continuously fluctuating loads over an extended period, due to cardiac pulsation. In addition, since the body represents an extremely corrosive environment for any implanted metal [2], the stent material must display good corrosion fatigue performance [3, 4]. Although stainless steels generally show a very good corrosion resistance in hostile environments, it has been known for a long time that the resistance can be reduced significantly under cyclic loading [5–8].

Since the interface between the host tissue and stent material plays an important role in stent biocompatibility, most advances in stent design have been focused on modifying the surface properties, including the surface finish [9]. Other studies [10, 11] have shown that the constitution and surface characteristics of the material may determine the nature of the host response and the long-term stent patency rate.

The chemical composition of the stent surface is dictated by the final processing steps during manufacture, and the rate of chemical and electrochemical reactions, that may later occur, is strongly dependent upon the properties of the passive layer formed on the stent surface. Under certain circumstances, the passivation layer can be broken down, and corrosion and consequently corrosion fatigue can occur, resulting in failure [10].

*Author to whom all correspondence should be addressed.

Stainless steels are self-passivating upon exposure to air and moisture, due to their high chromium content (>12%). Passivation treatments consist of chemically augmenting the naturally occurring protective oxide, by exposing it to highly oxidising conditions, e.g., dipping the metal in concentrated nitric acid. The passive layer formed, typically of the order of 30 Å in thickness, protects the base metal from further corrosion. This enhanced passive film is somewhat thicker and more persistent than that formed by self-passivation, due to the enhanced chromium fraction in the passive film resulting from selective dissolution of iron. With the presence of oxygen in the environment, the film can modify itself and can continue giving maximum protection in the case of the layer becoming altered or damaged. When conditions are favourable for maintaining passivity, stainless steels exhibit extremely low corrosion rates. If passivity is destroyed under conditions that do not permit restoration of the passive film, such as the conditions *in vivo*, then stainless steel will corrode much like a carbon or low-alloy steel.

Surface passivity is an essential requirement, but surface finish can also effect performance, with highly polished surfaces performing better in terms of corrosion and wear. Passivation of stent devices is enhanced by electropolishing and nitric acid passivation, and is an essential stage in the final processing of the stent device before it is sterilised and packaged. The importance and optimisation of this process is paramount to the long-term behaviour of these devices *in vivo*, and subsequently, their biocompatability.

Surface condition of the metal prior to passivation treatment is very important in achieving complete passivation, which cannot be achieved if the surface of the metal is not clean or contains surface defects. Elimination of these defects requires removal of the normal, protective oxide layers and 25–40 μm of the substrate metal via other techniques such as electropolishing. Electropolishing is characterised by smoothing of the surface of a metal to a mirror-finish by making it anodic in an appropriate electrolyte solution. The process is used industrially to polish a variety of metals [12].

Many studies have been performed on the effects of various surface treatment methods on the mechanical properties of different implantable metals, such as cold-working [13], shot peening [14–16], ion and plasma nitriding [17], induction hardening and carburising [18, 19]. Limited work is cited in literature on the effects of electrochemical surface treatments on the mechanical performance of stainless steels, the majority of this having been focused on high temperature applications. For an AISI 304 stainless steel tested at 593 °C, the low cycle fatigue life increased with improved surface finish due to an enhancement in the number of cycles to crack initiation [20]. A similar result has been reported in a Cr-Mo-V steel tested at 500 °C [21]. Wareing and Vaughan [22] have attributed the difference in fatigue life of machined and electropolished samples of 316 stainless steels tested at 400 °C to the different shapes of the cracks formed corresponding to the two surface conditions. In contrast Wood *et al.* [23] have observed no appreciable increase in fatigue life with surface finish in the same material at a higher temperature of 625 °C.

The work presented in this paper examines the effect of two different electrochemical surface treatments, (i.e., electropolishing and nitric acid passivation) on the static mechanical properties, high cycle fatigue and corrosion fatigue performance of a group of biomedical grade stainless steels. Four surface conditions are examined for both cold worked and annealed materials.

2. Materials and experimental procedures

2.1. Materials and surface treatments

The materials used for this study were 316LVM (meeting the ASTM F138-00 standard) in the cold worked condition, 316LSi in the annealed condition, both supplied by Sandvik Steel, UK, and 316L in the annealed condition supplied by RGB Stainless LTD., UK. As shown in Table I the most significant differences in the material compositions are the extremely low sulphur content in the 316LVM and the slightly higher silicon content in the 316LSi. Four different surface conditions were investigated:

1. As-machined samples, which were finished according to ASTM-E8M.
2. Samples electropolished in "Anapol 66".
3. Nitric acid passivated samples.
4. Samples electropolished and then passivated.

The actual electropolishing and passivation treatments applied to the samples were established by Costello [24].

2.2. Tensile testing method

Uniaxial tensile samples were machined from 4 mm diameter round bars, in accordance with ASTM standard E8M. Tensile testing was performed on a servohydraulic testing machine (INSTRON 4467) with a load capacity of 50 kN. Testing was carried out at room temperature at a speed of 0.2 mm/min, until fracture. A 12.5 mm gauge length extensometer was used to measure strain during testing. Two samples were tested from each surface treatment group, using the 316LVM and 316LSi materials. This primarily allowed the effects of cold working (316 LVM: cold worked, 316LSi: annealed) and surface treatment on the static mechanical properties to be assessed. As detailed in the introduction, static mechanical properties are important since

TABLE I Chemical composition in weight percent

Material	C	Si	Mn	S	P	Cr	Mo	Ni	N	Cu
316LVM	0.017	0.52	1.70	0.001	0.020	17.43	2.77	13.78	0.076	0.068
316LSi	0.015	0.8	1.91	0.011	0.022	18.22	2.62	12.44	0.045	0.16
316L	0.019	0.59	1.28	0.021	0.025	16.89	2.02	11.25	0.04	0.49

a stent undergoes considerable plastic straining during deployment.

2.3. Fatigue testing method

Hourglass fatigue samples with a minimum diameter of 4 mm were machined according to ASTM standard E466-96 and given a final maximum surface roughness of 0.2 μm. Samples were uniaxially tested using a Roell Amsler Vibrophore fatigue machine. Testing was carried out as a frequency of 120 Hz (natural frequency) with a load ratio of $R = 0.1$, in air, at room temperature. This tension-tension stress ratio was selected to prevent the thin samples undergoing compressive stresses and possibly buckling during testing. Two samples with each surface finish were tested at each stress level up to a maximum number of loading cycles of 1×10^7. The materials used were 316LVM and 316L. As for the static testing, the fatigue testing primarily allowed the effects of cold working (316LVM: cold worked, 316L: annealed) and surface treatment on the fatigue performance to be assessed. As detailed in the introduction, fatigue performance is very important since a deployed stent undergoes long-term cyclic loading. An assessment of the effects of cold work on the fatigue performance is of interest because, even though the undeployed stent is most usually in an annealed condition, the significant plastic strain during deployment could cause strain hardening.

Uniaxial, corrosion fatigue tests were carried out using the same testing machine, sample geometry, materials, frequency and R-ratio as above, the only difference being the presence of the corrosive environment. The tests were carried out in Ringer's solution maintained at 37 °C, (body temperature). Immersion of samples in the test solution was achieved by using a special purpose chamber surrounding the gauge length of the sample, made from a silicon tube [25]. The chamber was designed so as not to cause an additional load on the fatigue sample during the test. Leakage of solution from the chamber was prevented by using a special medical grade silicone sealant. Three litres of test solution were circulated around the sample at a flow rate of 2.0 l/min using a magnetically driven centrifugal pump. Fresh test solution was used after each test to ensure any corrosion products were removed from the circulation line. Temperature was maintained at 37 °C ± 1 °C.

3. Results and discussion

3.1. Static mechanical performance

Figs. 1 and 2 show the engineering stress/strain curves found for both materials after each surface treatment.

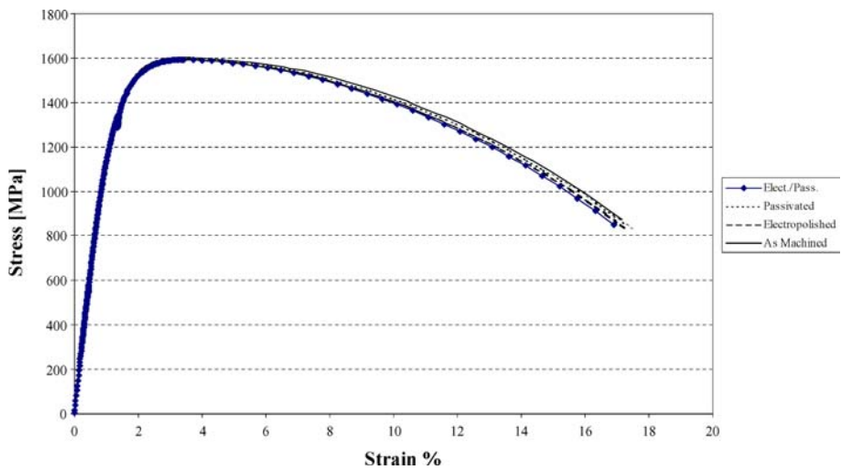


Figure 1 Engineering stress-engineering strain curves for 316LVM from tensile tests for different surface treatments.

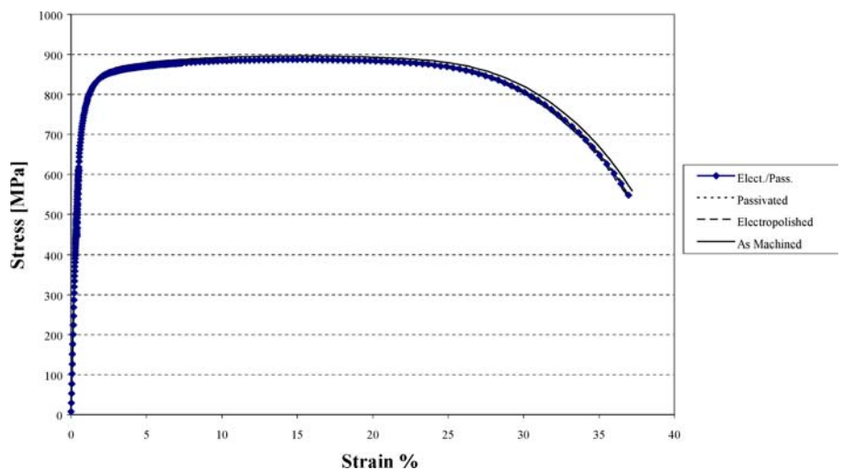


Figure 2 Engineering stress-engineering strain curves for 316LSi from tensile tests for different surface treatments.

TABLE II Selection of average mechanical properties for both 316LVM and 316LSi determined from tensile tests

Material and surface condition	0.2% proof stress (MPa)	UTS (MPa)	Elongation (%)
316LVM			
As-machined	1149	1602	17
Electropolished	1204	1600	17
Passivated	1200	1597	17
Elect./Pass.	1215	1602	17
316LSi			
As-machined	691	895	38
Electropolished	694	887	37
Passivated	695	892	36.8
Elect./Passiv.	678	887	37

TABLE III Surface roughness (Ra) values in μm for 316LVM and 316LSi samples

Surface condition	316LVM	316LSi
As-machined	0.220	0.223
Electropolished	0.136	0.108
Passivated	0.195	0.194
Elect./Passiv.	0.113	0.108

Table II summarises corresponding average mechanical properties. As can be seen, the surface treatments appear to have no effects on the static mechanical performance of either material. The mechanical properties calculated for both materials are consistent with their final processing conditions: the cold worked material, 316LVM, shows considerably higher proof stress and UTS values, with lower ductility, and the annealed material, 316LSi, shows lower yield and UTS values, but significantly higher ductility (>35%).

3.2. Surface roughness

The effects of the different surface treatments on test sample surface roughness is illustrated by the data for tensile samples reported in Table III; surface roughness measurements in microns (μm), obtained using white light interferometry (Newview 100 surface profiler) are given. It can be seen that the various surface finishes have a significant effect on the surface roughnesses, with the electropolished and electropolished/passivated groups resulting in the smoothest surfaces. The as-machined samples show roughness values that are twice those found for the smoothest sample set, with the passivated samples showing a slight improvement over the as-machined, with an average improvement in Ra of 11%.

3.3. Fatigue performance in air

S-N curves summarising the results of the fatigue tests in air (average cycles to failure for each stress level) are shown in Figs. 3 and 4. In these, and all the S-N curves presented in this paper, both the raw data points and curves determined using an empirical fit are presented. The results suggest a superior endurance limit for 316LVM (in the range 335 and 350 MPa) in comparison to 316L (in the range 290 and 305 MPa). This is expected given that the 316LVM material was received in the worked condition, compared to the annealed 316L. It is well known and documented that fatigue strength properties, like static properties (Table II), are for many alloys affected by heat treatment procedures and mechanical working [27]. Significantly, the data does not suggest a strong dependence of endurance limit on surface treatment, for either material.

The electropolish and electropolish/passivation surface treatments do have noticeable effects on increasing fatigue lives for stress levels above the endurance limit, whereas the passivation treatment has only a very small effect. Where any slight improvements are observed due to passivation, these could be explained by the removal of surface inclusions, such as manganese sulphides, as a result of the nitric acid dissolution, which are thought to be potential initiation sites for fatigue [28–30]. In terms of distinguishing between the electropolish and electropolish/passivation surface treatments, it can be said that no conclusive improvement in fatigue performance is observed for passivation following electropolishing, in comparison to electropolishing alone. In overall terms, the data strongly suggests that the electropolishing is the key treatment in influencing fatigue lives for these materials.

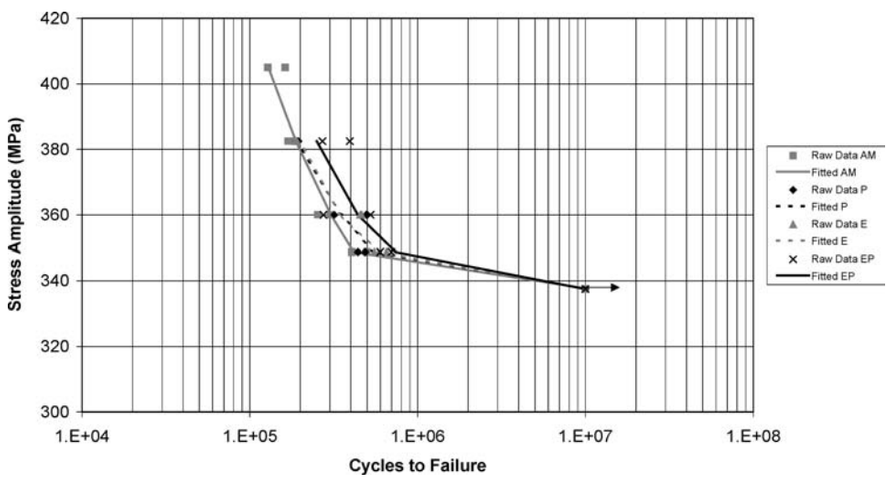


Figure 3 Comparison of fatigue lives in air for different surface finishes for 316LVM. As-machined (AM), electropolished (E), passivated (P) and electropolished and passivated (E/P).

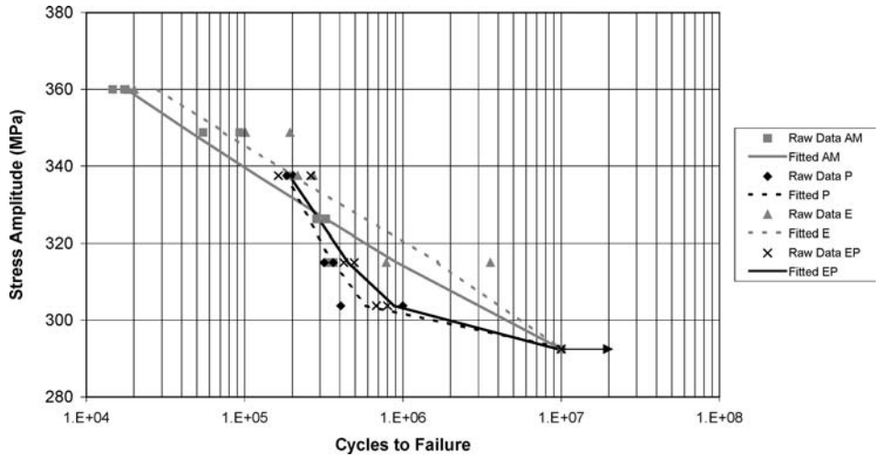


Figure 4 Comparison of fatigue lives in air for different surface finishes for 316L. As-machined (AM), electropolished (E), passivated (P) and electropolished and passivated (E/P).

The results found here are contrary to the work carried out by Field and Kahles [26], who reported a 12% decrease in fatigue strength for an electropolished 4340 stainless steel, when compared to gentle grinding. Wood *et al.* [23] argued that the reduction in fatigue strength was experienced because the fatigue enhancement produced by the compressive stresses associated with low-stress grinding had been removed by the electropolishing treatment. The increase in fatigue life for samples that underwent electropolishing treatments in this work can be attributed to the reduction in surface roughness and hence the reduction in surface stress concentration levels. The results reported here are in agreement with those of Thompson *et al.* [24] and Basiniski *et al.* [25] who found that by the elimination of surface roughness through electropolishing, fatigue life was significantly increased.

3.4. Corrosion fatigue performance

S-N curves summarising the results of the fatigue tests in the corrosive environment (average cycles to failure for each stress level) are presented in Figs. 5 and 6. The results follow a similar pattern to that seen for fatiguing in air. The electropolishing and electropolishing/passivation treatments have noticeable effects in terms of improving fatigue lives, whereas passivation on its own has a very small effect. As proposed for fatiguing in air, any slight improvements in fatigue lives found for passivated samples are likely to be a result of the removal of manganese sulphide inclusions.

Figs. 7 and 8 show a selection of the S-N curves, already presented in Figs. 3 to 6, in a format that allows for direct assessment of the effects of fatiguing in the corrosive environment relative to fatiguing in air. Examination of the full set of fatigue data, for both materials and for the four surface finishes, (for which Figs. 7 and 8 present a representative sample) shows that the fatigue performance of both materials, regardless of the surface finish, is significantly impaired if they are cycled in the corrosive environment instead of in air. It would seem also that the endurance limit for the materials has been significantly reduced in the corrosive environment; certainly no tendency towards an endurance limit is evident for either material for the stress range tested. Similar findings have also been reported for 316L and mild steels in aqueous environments [33–36]. The results

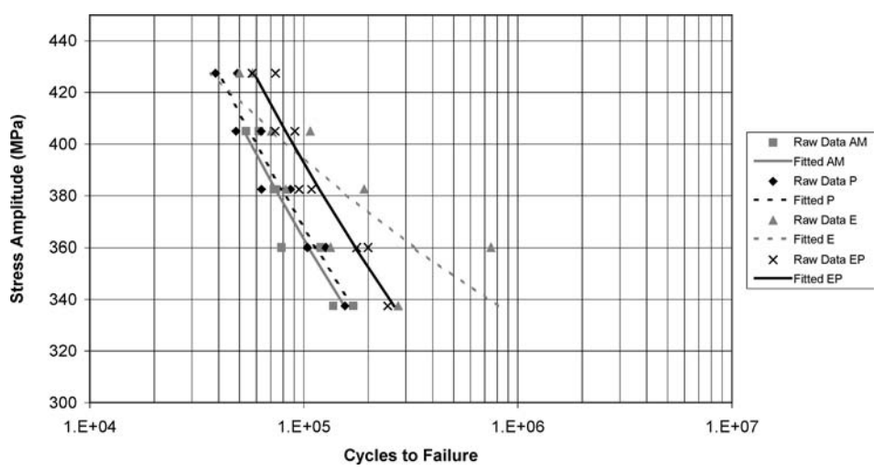


Figure 5 Comparison of fatigue lives in a corrosive environment for different surface finishes for 316LVM. As-machined (AM), electropolished (E), passivated (P) and electropolished and passivated (E/P).

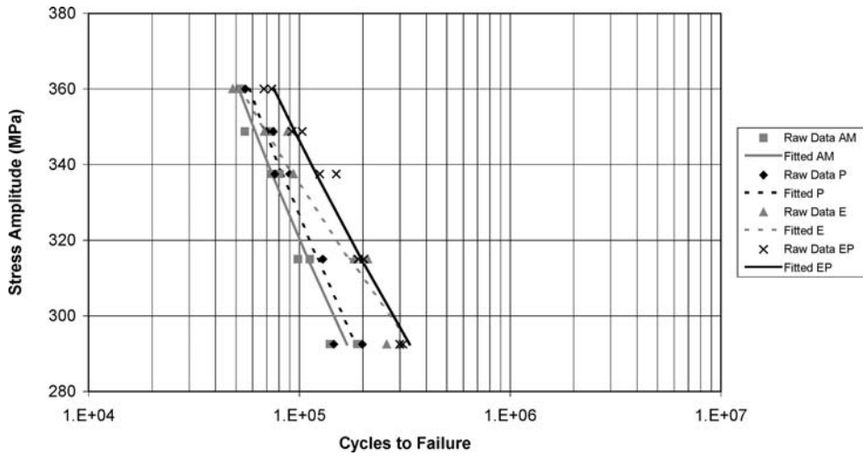
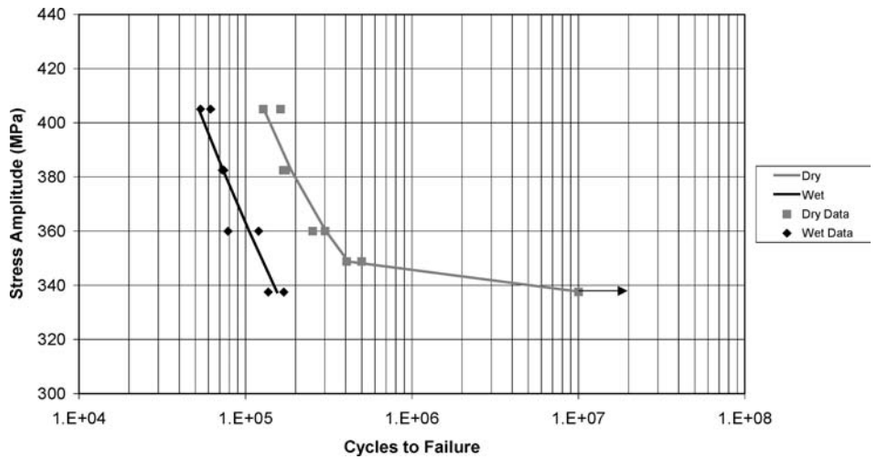
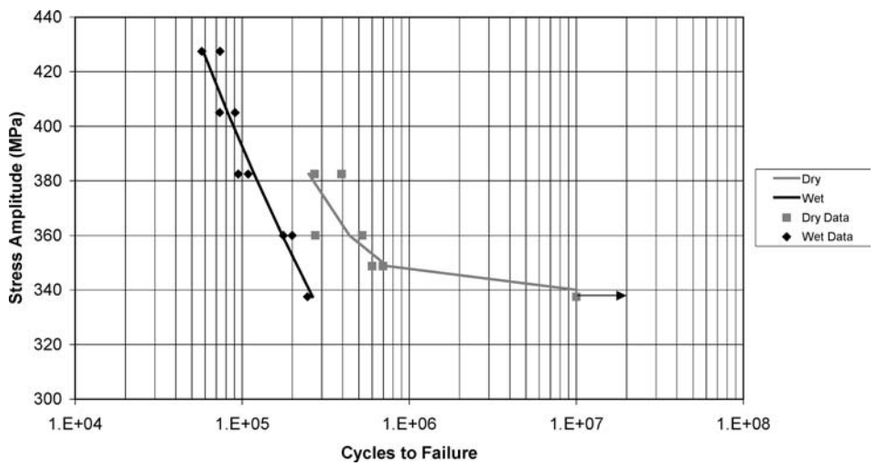


Figure 6 Comparison of fatigue lives in a corrosive environment for different surface finishes for 316L. As-machined (AM), electropolished (E), passivated (P) and electropolished and passivated (E+P).



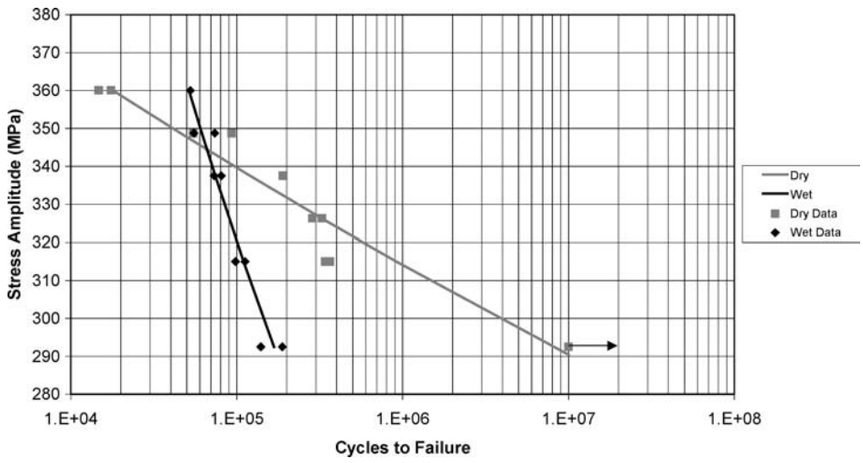
(a)



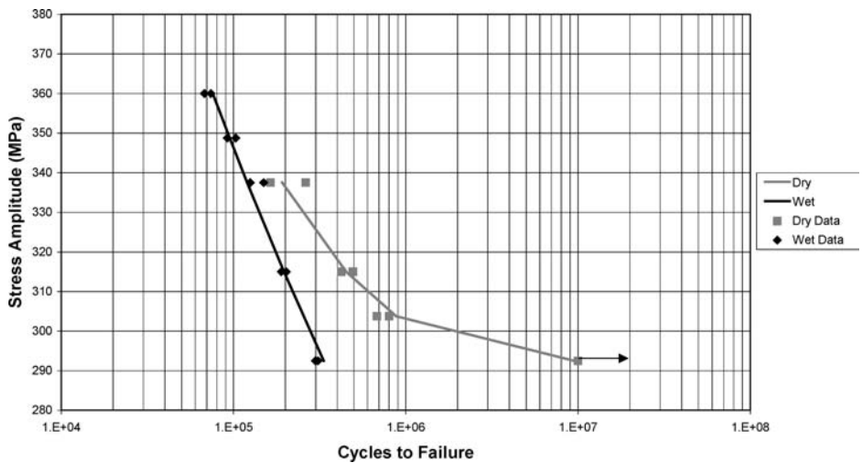
(b)

Figure 7 Comparison of fatigue lives in wet and dry conditions for 316LVM (a) as-machined and (b) electropolished and passivated.

also suggest that for 316LVM the reductions in fatigue lives do not depend strongly on the surface finish. For 316L, a certain dependence is noticable, with the as-machined samples showing the largest reductions and the electropolished/passivated samples showing the smallest reductions, in overall terms, as is illustrated in Fig. 8. One final point is that the magnitudes of the fatigue life reductions are not hugely different for either material, which does not indicate a strong dependence of fatigue life reduction on material composition



(a)



(b)

Figure 8 Comparison of fatigue lives in wet and dry conditions for 316L (a) as-machined and (b) electropolished and passivated.

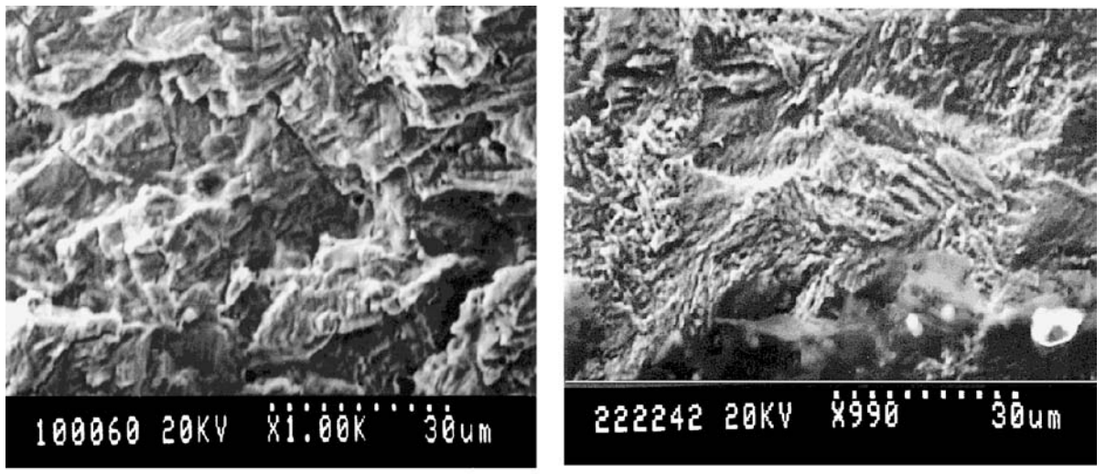
and final processing state, i.e., cold-worked versus annealed.

Reductions in fatigue life of up to 90% have been reported for a high strength steel in salt water [37]. Other works report on the reduction in fatigue life but do not quantify this [3, 33, 34, 38]. Many reasons have been reported for the consistent reduction in fatigue lives when cycled in a corrosive environment including, differences in oxygen concentration that impede the repassivation process [38–40], non-metallic inclusions and pit formation [41, 42], instability of the passivation layer [36] and a reduction in surface energy [43]. It is well known and documented that when passivated metals are subjected to extremely corrosive environments (for example, conditions *in vivo*), the heterogeneous film is attacked and chemical reduction occurs [44].

3.5. Fatigue fracture surfaces and exterior surface damage

A systematic scanning electron microscopic investigation of the fatigue samples was performed following testing. Fracture surfaces were compared and exterior surface damage was assessed. Fig. 9(a) and (b) show representative micrographs of 316L, fatigued at 700 MPa in both air and corrosive fluid, respectively, taken at the same magnification. Close examination of the 316L sample fatigued in the corrosive fluid (Fig. 9(b)) reveals a more faceted surface with a greater surface area than that for the samples fatigued in air (Fig. 9(a)), which indicates the interaction of the corrosive fluid with the material surface. Fig. 9(b) appears to show slight evidence of embrittlement in 316L when fatigued in the corrosive environment, which is associated with an intergranular fracture type surface [13]. Embrittlement facilitates the formation of fatigue cracks, and corrosion interaction at the crack tip increases the crack growth rates [45]. No indication of embrittlement in the 316LVM material was observed when fracture surfaces were compared in air and the corrosive fluid.

Examination of the crack initiation sites of samples from both materials fatigued in air showed evidence of small notches at the crack origin site in most cases. This tended to be more pronounced in the 316L material than the 316LVM material. As the maximum stress increased, a more pronounced final fracture occurred,



(a) (b)

Figure 9 (a) SEM of 316L fracture surface, fatigued in air and (b) SEM of 316L fracture surface, fatigued in corrosive environment.

particularly for the 316L material, with multiple void formation on the fracture surface. This may have been a result of static modes of failure (void growth and coalesence) becoming more evident at the higher stress values [45]. This was not nearly so noticeable for 316LVM, where there was very little evidence of voids on the fracture surface, even at higher stress levels. The higher stress levels employed for this material may not have been high enough for static modes of failure to become evident. Examination of failed samples for both materials did not show much of a dependence of fracture surface on sample surface treatment (as-machined vs. electropolished, etc.).

The circumferences of all samples fatigued in a corrosive environment were examined for the presence of pits and secondary cracks (cracks other than the main crack that resulted in failure). Similar to samples fatigued in air, the extent of damage observed was significantly more pronounced for the 316L material when compared to the 316LVM material. Table IV summarises the general appearance of each sample tested for both materials at different stress levels and for each different surface finish. The level of pitting and secondary cracking has been graded as follows:

TABLE IV Characterisation of the appearance of the failed regions (lateral surfaces close to fracture site) of corrosion fatigue samples, with severity of damage graded as defined in the text

Max Stress (MPa)	As-machined	Electropolished	Passivated	Elect./Passiv.
316LVM				
750	0	0	0	0
800	0	0	0	0
850	1	0	1	0
900	1	1	1	1
950	2	1	1	1
316L				
650	0	0	0	0
700	1	1	1	0
750	3	2	2	2
775	4	4	4	3
800	5	5	5	5

Grade 5: Multiple pitting and secondary cracking
Grade 4: Some pitting and secondary cracking
Grade 3: Slight evidence of pitting and secondary cracking
Grade 2: Pitting, no cracks
Grade 1: No pitting, but some secondary cracking
Grade 0: No evidence of any pitting or secondary cracking

With reference to Table IV, the extent of damage observed is significantly more pronounced for the 316L material when compared to the 316LVM material. At stresses of 700 MPa, pitting and secondary cracking were evident in 316L; Fig. 10 shows an electropolished 316L sample fatigued at 800 MPa and the damage is clearly evident. On the other hand, the 316LVM

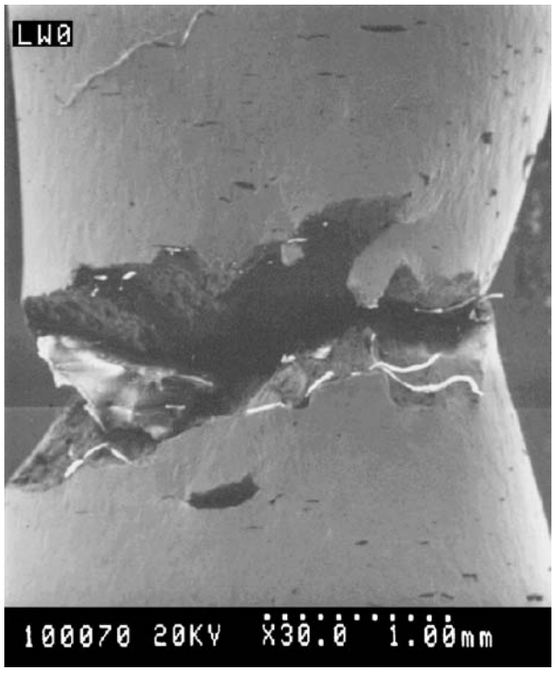


Figure 10 SEM of 316L (electropolished) fatigued at 800 MPa.

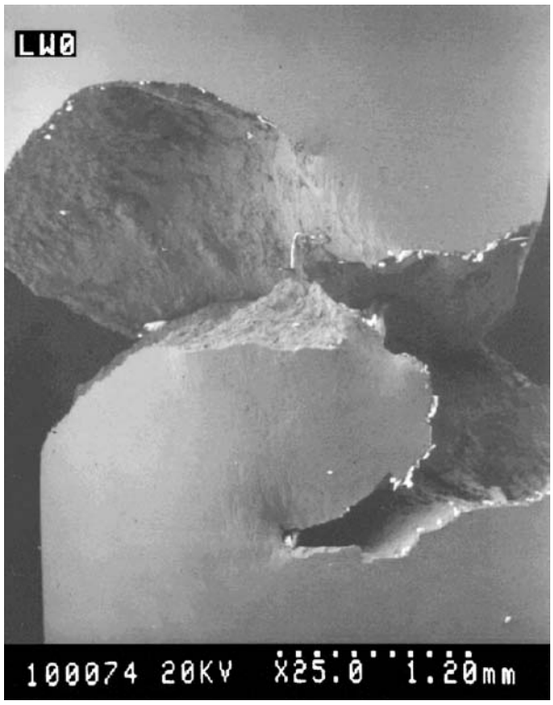


Figure 11 SEM of 316LVM (electropolished) fatigued at 950 MPa.

material exhibited no evidence of secondary cracking at stresses lower than 850 MPa. Even at higher stresses, only slight secondary cracking occurred. Also, no pitting was found for the 316LVM material at any stress level. Fig. 11 shows an electropolished 316LVM sample fatigued at the highest stress level used for these materials, 950 MPa, and the absence of pitting and secondary cracking is evident.

As mentioned, evidence of pitting was prominent in the 316L material, especially as the maximum stress level increased. Fig. 12(a) shows a close up of the failed region of 316L as-machined (800 MPa) showing the presence of multiple pit sites. Closer examination of such pits showed evidence of the presence of inclusions in the majority of the pits. This can be justified by the high content of sulphur present. 316L contains 0.021 wt% sulphur and 316LVM containing 0.001 wt%. The presence of sulphur can result in the formation of sulphides (non-metallic inclusions, especially manganese sulphide) during processing. Pitting at sulphide inclusions in corrosive environments (in the presence of chlorine ions in particular) is known to occur and to produce favourable sites for corrosion fatigue crack initiation [41, 46]. In the present study a large number of samples were examined in the SEM, and EDS analysis of visible inclusions indicated that only manganese and sulphur were present. Surface geometrical irregularities and locations of passivation layer fracture/breakdown could also serve as pit formation sites. The latter would correlate with the observed increase in surface pit formation as the stress level is increased.

The presence of inclusions in the material has been further confirmed by examination of the fracture surfaces of the 316L material samples. Fig. 12(b) shows inclusions, which are more than likely sulphides and carbides, found in the ductile dimples on the final fracture surface of a 316L material sample. Similar microstructures as the one presented in Fig. 12(b) were reported in [47] and the inclusions were found to be sulphides. The fact that the inclusions are present on the fracture surface means that they play a significant role in the final ductile fracture of the samples, through

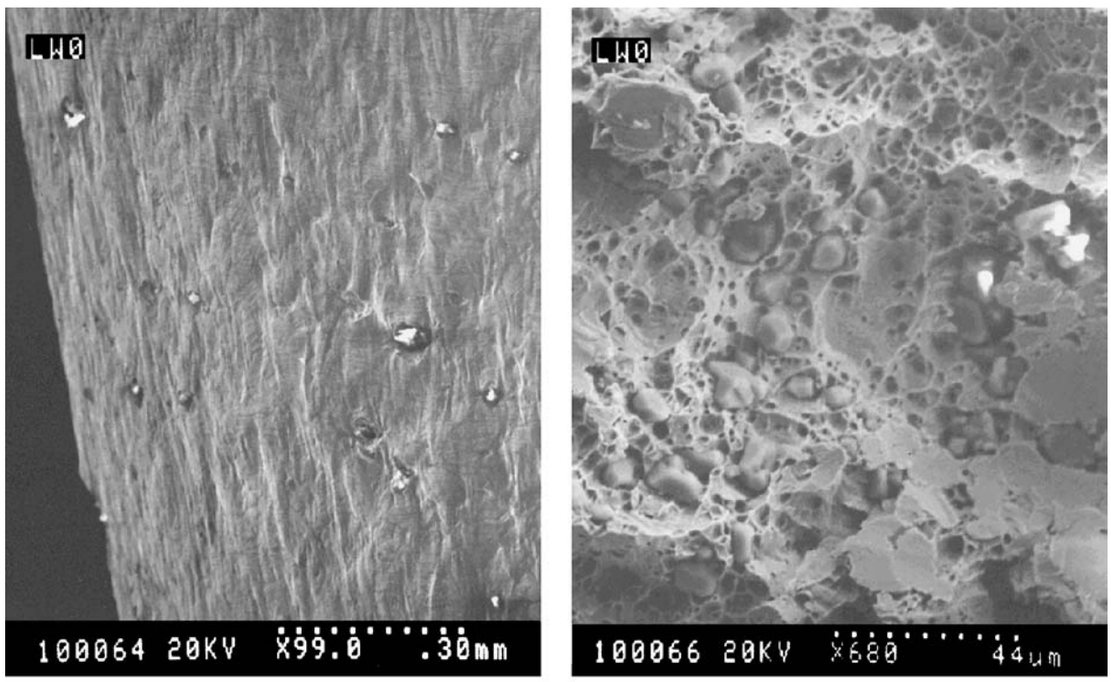


Figure 12 SEMs of 316L (as-machined) fatigued at 800 MPa, (a) multiple pit sites and (b) sulphide inclusions in a ductile dimpled fracture surface.

void initiation at sites of matrix/inclusion interface debonding or inclusion cracking.

The importance of inclusions and pits for fatigue crack initiation in the 316L material in a corrosive environment is in agreement with conclusions of Meuller [48] and Kahni and Dengel [49]. The prevalence of inclusions and pits also explains the reduction in the fatigue life of this material for testing in a corrosive environment relative to testing in air. In addition, as can be seen from Table IV, the greater severity of damage for the as-machined samples, in comparison to the electropolished/passivated samples, correlates with the greater reduction in fatigue lives for the former in comparison to the latter, as shown in Fig. 8.

No obvious failure mechanism for the 316LVM material could be found on any of the samples examined. There was no evidence of secondary cracking away from the failed region. Given that there was almost no evidence of pit or crevice corrosion (Table IV), failure is most likely due to:

1. the formation of slip bands as a result of high local alternating plastic strain amplitude, which would result in the rupture of the protective oxide film and the generation of surface notches and corrosion fatigue crack initiation sites, or
2. preferential dissolution due to electrochemical differences between locally high and low stressed areas, which is possible given that the material is coldworked and contains microscale residual stress distributions, which in turn would generate surface notches.

For the 316LVM fatigued in the corrosive environment, the absence of damage for all surface finishes, correlates with the observation (Fig. 7) that fatigue life reduction is relatively independent of surface finish.

It is striking that although the fatigue performance of 316L in a corrosive environment appears much worse at the micro level than 316LVM, both materials experience relatively similar fatigue life reduction magnitudes, across the stress ranges tested (Figs. 7 and 8). This would imply that even though the evidence of pitting is very strong for the 316L in the corrosive environment, this does not translate into fatigue crack inita-tion mechanisms that are significantly more effective, in terms of reducing fatigue lives, than those present in the 316LVM material in the same environment. It may be the case that even though the 316LVM is much lower in sulphur, hence not suffering from the sulphide formation problem, the presence of high local residual stresses due to cold work could result in a fatigue crack initiation mechanism, based on preferential dissolution, that is equally effective in the corrosive environment.

4. Summary and conclusions

Medical grade stainless steels were subjected to three different electrochemical surface treatments, viz., passivation, electropolishing, and electropolishing and passivation, and were then mechanically tested. The treatments were found to have a significant effect on the surface roughness (Ra) of the samples, with the electropolished/passivated combination resulting in the smoothest surfaces.

316LVM (work hardened) and 316LSi (annealed) were subjected to static loading and the surface treatments were found to have no effect on the mechanical performance. 316LVM (work hardened) and 316L (annealed) were subjected to fatigue loading in air and in a corrosive environment (Ringer's solution). For both the wet and dry fatigue tests the surface treatments had a significant effect on fatigue lives, with the electropolished and the electropolished/passivated groups showing the best overall performance for both materials. Passivation on its own produced no great improvement in fatigue performance. Fatiguing in the corrosive environment produced a reduction in the fatigue properties (fatigue lives and endurance limits) in all cases. The magnitude of the reduction seemed to be quite similar for both materials. For the 316LVM the reductions seemed independent of the surface finish, whereas for the 316L the surface finish did seem to contribute in that the electropolished/passivated samples showed smaller reductions that the as-machined samples.

SEM examination of fatigue fracture surfaces showed slight evidence of embrittlement in 316L when fatigued in the corrosive environment, although none was evident on 316LVM samples. Surface pits were thought to be the main sites responsible for initiation of fatigue cracks for the 316L in the corrosive environment; pits and inclusions were clearly evident under SEM examination. For the 316LVM no apparent mechanism of corrosion fatigue failure could be definitively identified, although possible mechanisms were proposed, including preferential dissolution in areas of non-uniform residual stresses. Given this difference, the relative similarity in fatigue life reduction in going from dry to wet environments for both materials showed the relative similarity in effectiveness of the different active mechanisms.

In overall terms this work shows that surface treatments of the type considered here do not affect static mechanical properties and so in the case of stent they would not influence ductility levels, as would be important in stent deployment, where considerable plastic deformation is produced.

The surface treatments do have significant effects on fatigue performance, which is important in terms of the long-term physiological loading of the stent. The results confirm that electropolishing and passivation do have positive effects on fatigue lives. The surface treatments, however, cannot counteract the strongly negative effect of a corrosive environment, with significant reductions in fatigue lives being noted across the full range of materials and surface treatments examined.

The 316LVM (work hardened) consistently performed better than the 316L (annealed) in both fatigue life and in microscale damage levels, which is due to a combination of the work hardening and the lower sulphur levels for the 316LVM.

Acknowledgments

The authors wish to acknowledge financial support for this work from the Higher Education Authority—HEA. P. McHugh wishes to thank Dr. T. Connolley for very valuable discussions, input and information.

References

1. B. P. MURPHY, P. SAVAGE, P. E. McHUGH and D. F. QUINN, *Ann. Biomed. Engng.* **31**(6) (2003) 686.
2. K. HAYASHI, *JSME Int. J.* **30** (1987) 1517.
3. Y. HIGO and Y. TOMITA, *Corros. Sci.* **35** (1993) 587.
4. K. HAYASHI, *J. Soc. Mater. Sci. Jpn.* **43** (1994) 1502.
5. M. KAKAJIMA, T. SHIMUZU, T. KANAMORI and K. TOKAJI, *Fat. Fract. Eng. Mater. Struct.* **21** (1998) 35.
6. H. J. GOUGH, *J. Inst. Metals* **49** (1932) 17.
7. D. J. Jr. MCADAM, *Proc. ASTM* **41** (1941) 696.
8. B. B. WESCOTT, *Mech. Engng.* **60** (1938) 813.
9. C.-C. SHIH, S-J. LIN, K-H CHUNG, Y-L CHEN and Y-Y. SU, *J. Biomed. Mat. Res.* **52** (2) (2000) 323.
10. O. F. BERTRAND, R. SIPEHIA, R. MONGRAIN, R. RHODES, J. C. TARDIF, L. BILODEAU, L. G. COTE and M. G. BOURASSA, *J. Am. Coll. Cardiol.* **32** (1998) 562.
11. J. C. PALMAZ, *Texas Heart Inst. J.* **24** (1997) 156.
12. L. C. MARSLAND and G. T. BURSTEIN, *Electroc. Comm.* **2** (2000) 591.
13. M. PAPAKYRIACOU, H. MAYER, C. PYPEN, H. PLENK and S. STANZL-TSCHEGG, *Int. J. Fat.* **22** (2000) 873.
14. S. S. MANSON, *ASTM STP* **495** (1971) 254.
15. S. SURESH, "Fatigue of Materials" (Cambridge University Press, New York, 1988).
16. V. SCHULZE, K. H. LANG, O. VOHRINGER and E. MACHERAUCH, *Proc. Int. Conf. on Shot Peeing ICSP* **6** (1996) 403.
17. N. E. FROST, K. J. MARSH and L. P. POOK, in "Metal Fatigue" (Clarendon Press, Oxford, 1974) p. 121.
18. R. W. LANDGRAF and R. A. CHERNEKOFF, *ASTM STP* **1004** (1988) 1.
19. R. W. LANDGRAF and R. H. RICHMAN, *ibid.* **569** (1975) 130.
20. P. S. MAIYA and D. E. BUSCH, *Metall. Trans.* **6A** (1975) 1761.
21. J. H. RYU and S. W. NAM, *Int. J. Fat.* **11** (1989) 433.
22. J. WAREING and H. G. VAUGHAN, *Met. Sci.* **13** (1979) 1.
23. D. S. WOOD, J. WYNN, A. B. BALDWIN and P. O'RIORDON, *Fat. Fract. Eng. Mater. Struct.* **3** (1980) 39.
24. E. COSTELLO, "A Study of Passivation Processes Applied to Stainless Steels for Use in the Biomedical Industry," Ph.D. Thesis, NUI, Galway, Ireland (2003).
25. L. M. WELDON, "The Effects of Passivation Processes on the Mechanical Performance of Stainless Steels for Stent Applications," M.Eng.Sc. Thesis, NUI, Galway, Ireland (2001).
26. J. A. COLLINS, in "Failure of Materials in Mechanical Design," 2nd Ed. (John Wiley & Sons, 1993) p. 374.
27. G. HULTQVIST and C. LEYGRAF, *Corrosion (NACE)* **36** (1980) 126.
28. G. SALVAGO and G. FUMAGALLI, *Corros. Sci.* **36** (1994) 733.
29. Z. SZKLARSKA-SMIALOWSKA, "Pitting Corrosion of Metals" (NACE, Houston, TX, 1986).
30. M. FIELD and J. F. KAHLES, *STC S* **20** (1971) 107.
31. N. THOMPSON, N. J. WADSWORTH and N. LOUAT, *Philosophical Magazine* **1** (1956) 113.
32. S. J. BASINSKI, Z. S. BASINSKI and A. HOWIE, *Philosophical Magazine* **19** (1983) 899.
33. M. TAIRA and J. LAUTENSCHLAGER, *J. Biomed. Mat. Res.* **26** (1992) 1131.
34. M. MORITA, T. SASADA, I. MONURA, Y.-Q. WEI and Y. TSUKAMOTO, *Ann. Biomed. Engng.* **20** (1992) 505.
35. A. D. WILSON, *ASM Handbook—Fatigue and Fracture* **19** (1996) 591.
36. Y. HIGO and Y. TOMITA, *ASTM STP* **1173** (1994) 148.
37. F. FORREST, "Fatigue of Metals" (Pergamon, 1962).
38. M. MORITA, T. SASADA, H. HAYASHI and Y. TUKAMOTO, *J. Biomed. Mat. Res.* **22** (1988) 529.
39. S. H. TEOH, *Int. J. Fat.* **22** (2000) 825.
40. M. NIINOMI, *Mat. Sci. & Eng.* **A243** (1988) 231.
41. G. MURTAZA and R. AKID, *Eng. Frac. Mech.* **67** (2000) 461.
42. Y. R. QIAN and J. R. CAHOON, *Corr. Sci.* **53** (1977) 129.
43. P. LUKAS, *ASM Handbook—Fatigue and Fracture* **19** (1996) 97.
44. D. ASKELAND, in "The Science and Engineering of Materials" (PWS Publishers, Boston, 1985) p. 507.
45. H. MAYER, *Int. Mat. Rev.* **44** (1994) 1.
46. "Metals Handbook 2nd Ed." (The Materials Information Society ASM International, 1998) p. 1214.
47. M. P. MEULLER, *Metals Technol.* **9** (1982) 587.
48. M. K. KHANI and D. DENGEL, *Metal Trans.* **27A** (1996) 133.

Received 24 November 2003
and accepted 20 July 2004