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The influence of surface condition on the localized corrosion of 316L stainless steel orthopaedic implants

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The localized corrosion of austenitic stainless steel 316L intended for use as orthopaedic implants is determined as a function of the surface condition and metallurgical state. From the examination of samples exposed to a ferric chloride solution, at both 22 and 37 °C, the independent contribution of crevice and pitting corrosion to localized corrosion is determined. Both forms of localized corrosion occur to a greater extent at the higher temperature. The results indicate that weight loss measurements may not be sufficient to determine the extent of crevice corrosion separately from the influence of pitting corrosion. More importantly, the surface conditions required for the best resistance to crevice or pitting corrosion differ. Electropolished surfaces provide the best resistance to crevice corrosion, while ''bead blasted'' surfaces provide the best resistance to pitting corrosion. The implication of this result in terms of the serviceability as orthopaedic implants is discussed. The current results indicate the cold-worked state exhibits improved resistance to pitting corrosion. However, the influence of the metallurgical state could not be separated from a possible compositional effect.

1. Introduction

Type 316L stainless steel is the most popular metal for use as osteosynthesis plates for orthopaedic applications. This popularity stems from a satisfactory combination of good mechanical properties and reasonable cost. However, during exposure to physiological environments the protective surface oxide inherent to 316L is not stable [1], causing both crevice and pitting corrosion to occur [1–3]. Analysis of retrieved implants reveals that even after exposure times as short as 2 months crevice corrosion is evident [4]. While it is uncommon for the pitting and crevice corrosion to be sufficiently extensive that mechanical failure occurs, corrosion releases metallic ions into surrounding tissue leading to inflammation and possible loosening of the implant [5]. Furthermore, there is concern regarding the accumulation of metallic ions, released by corrosion, within internal organs [6]. Pitting and crevice corrosion have resulted in the premature removal of 316L implants [4].

In light of the foregoing, the localized corrosion of 316L for orthopaedic applications has been extensively studied. It is well established that the initiation of both pitting and crevice corrosion is associated with the presence of sulfides [7, 8]. As a consequence the maximum sulfur content of 316L for implant applications is 0.01 wt % [9]. The surface condition of the implant also has a major influence on the resistance to localized corrosion. Generally, reducing the average crevice gap increases the susceptibility to crevice corrosion [10]. However, surface grinding may be detrimental to crevice initiation [11], since it produces residual surface stresses, while electropolishing improves corrosion due to the reduced surface area, removal of the disturbed layer left by grinding, removal of imbedded contaminants, and development of a protective surface film [1, 2, 11].

Type 316L bone fixture plates can be implanted in either the cold-worked or annealed condition. The former provides higher strength, but during surgical procedures the latter is more easily formed to bone contours. Previous investigations suggest that the cold-worked condition is more susceptible to crevice corrosion [2, 12], probably due to an increase in the internal stress.

The purpose of the work presented in this paper is to determine the susceptibility to pitting and crevice corrosion at 22 and 37 °C of 316L surfaces prepared according to industrial practices for bone fixture plates. Accordingly, the results for five surface conditions are presented for both the cold-worked and annealed states. A limited number of samples of 304 are included for comparison.

2. Materials and experimental procedure

Approximately 50 316L samples with dimensions of $25 \times 50 \times 5.5$ mm were supplied by a manufacturer of orthopaedic bone fixture plates. The samples were prepared from either annealed or cold-worked stock,

TABLE I Composition of 316L samples (weight per cent)

Condition	C	Mn	Si	P	S	Cr	Ni	Mo	Cu	N
Annealed	0	1.48	0.49	0	0	17.5	13.5	2.11	0.3	0
Cold-worked	0	1.75	0.4	0	0	17.5	14.9	2.79	0	0

TABLE II Properties of 316L samples

Condition	0.2% Yield Strength MPa	Ultimate Tensile Strength MPa	% Elongation	Hardness	ASTM grain size
Annealed	503	665	41	179 BHN*	7–8
Cold-worked	945	993	13	28 HRc	9

* BHN = Brinell Hardness Number; HRc = Rockwell C Hardness

with the compositions and properties listed in Tables I and II. The sample surfaces to be tested were prepared according to one of the following procedures:

- A — annealed condition, with no surface modification applied to mill finish
- CW — cold-worked condition, with no surface modification applied to mill finish
- 120 — surface ground with 120 grit emery paper
- V — surface modified in a vibratory polisher
- B — surface manually hand buffed
- BB — surface modified by impingement with glass beads (''bead blasted'')
- EP — electropolished.

Accordingly, a sample identified as CW/B/EP is in the cold-worked state, was hand buffed followed by electropolishing. The details of the surface preparation procedures are proprietary. To characterize the sample surfaces a profilometer was used to determine the average surface roughness.

The susceptibility to pitting and crevice corrosion was determined by using a test procedure based on the ferric chloride immersion test of ASTM G48, Method B [13]. This test standard indicates that surfaces are to be ground to 120 grit finish. However, for the current work surface finish is a major independent variable, so only a limited number of samples were ground to a 120 grit finish. Also, a multiple crevice geometry was utilized. This consisted of machining 1.5 mm square grooves across the diameter of the end faces of the Teflon cylinders to form 16 crevice sites per sample. The sample geometry during testing is illustrated in Fig. 1. Each sample was immersed in a test tube containing 150 ml of 6% ferric chloride solution for 72 h. The resulting pitting and crevice corrosion was quantified by weight loss measurements, pit density and size, and the percentage of crevice sites corroded.

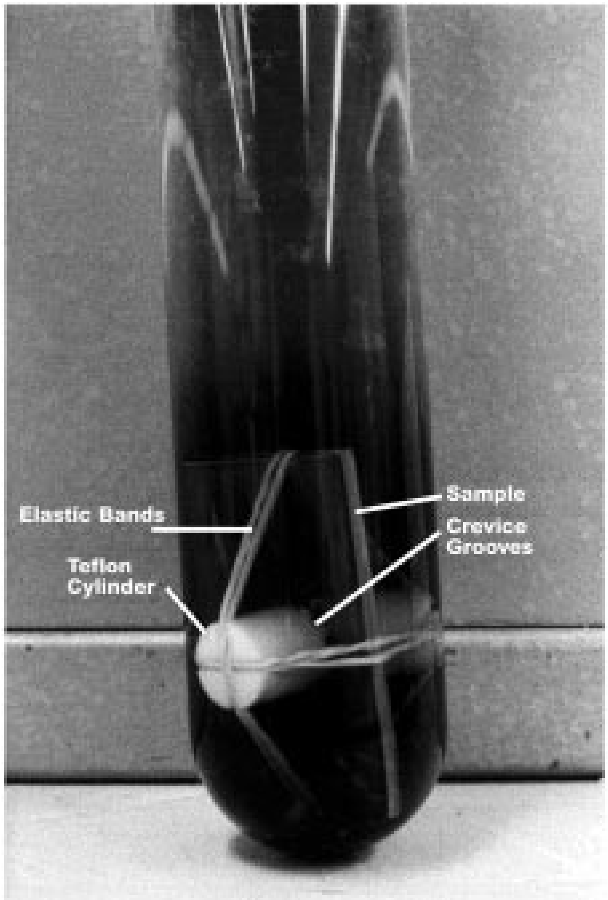

Figure 1 Sample immersed in ferric chloride solution illustrating geometry of crevices between sample and Teflon cylinder.

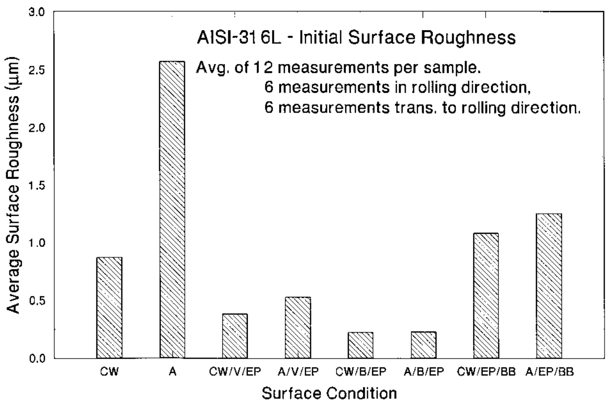

Figure 2 Average surface roughness of prepared surfaces prior to immersion testing.

3. Results
3.1. Surface roughness
The average surface roughness of the prepared samples is plotted in Fig. 2. The most significant result is that the annealed condition (A) has an anomalously rough surface. However all the surface modification procedures virtually eliminated this initial difference between the cold-worked and annealed conditions. Finishing by electropolishing (EP) provided the smoothest surfaces,

with the hand buffing (B/EP) prior to electropolishing giving slightly smoother surfaces than the vibratory polishing (V/EP). Bead blasting (BB) produces surfaces that are rougher than the as-received cold-worked (CW) surface.

3.2. Weight loss

Examination of the samples revealed that no general corrosive attack occurred. Crevice corrosion occurred between the teflon and stainless steel surfaces, and between the elastic bands and the sample edges. Pitting attack occurred on the transverse edges of some samples. The crevice and pitting corrosion results are presented in subsequent sections.

The average weight loss during the 72-h immersion tests as a function of the surface roughness is presented in Fig. 3. At the 22 °C test temperature the weight loss increases with increasing surface roughness, except for the anomalously rough annealed condition. However, at 37 °C this trend is not evident. Fig. 4 plots the average weight loss versus the initial surface condition. The smooth surfaces of the samples for which electropolishing (EP) was the final step resulted in the lowest weight loss during 22 °C tests. However, in terms of weight loss, no advantage accrues from the smoother electropolished surfaces at 37 °C. Similar to Fig. 3, no clear trends are evident from the weight loss results at 37 °C.

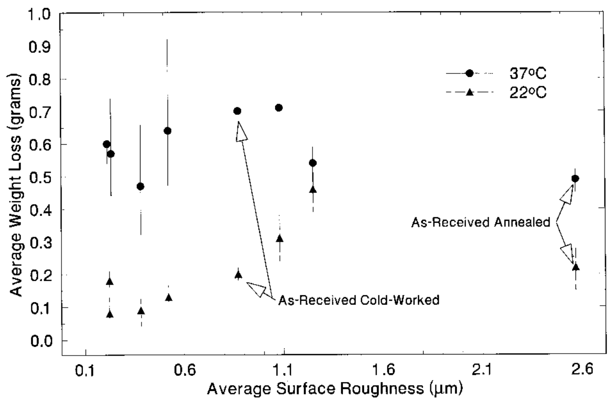

Figure 3 Weight loss as a function of surface roughness after 72 h immersion in ferric chloride.

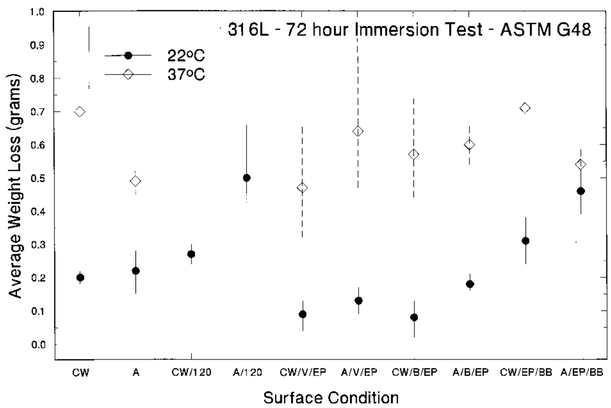

Figure 4 Weight loss as a function of surface condition after 72 h immersion in ferric chloride.

The results of Figs 3 and 4 illustrate that weight loss measurements do not delineate the influence of surface condition on the localized corrosion of 316L at 37 °C. Moreover, the weight loss measurements provide no differentiation between crevice attack and pitting attack. Consequently, the extent of crevice and pitting corrosion are characterized separately in the following sections.

3.3. Crevice corrosion

To separate the susceptibility to crevice corrosion from pitting corrosion the percentage of crevice sites exhibiting corrosion was evaluated for each surface condition. Only crevice sites between the Teflon cylinder and sample (identified in Fig. 1) were included in this analysis, since on some samples the transverse edges can have a different surface topography. The results of this analysis are shown in Fig. 5, from which several trends are evident.

As expected for all surface conditions, the percentage of crevice sites corroded increased significantly on increasing the temperature from 22 to 37 °C. Also, as expected, at both temperatures type 304 suffers severe attack. Both the cold-worked (CW) and annealed (A) conditions exhibit a similar percentage of crevice sites attacked at 22 °C, with the annealed condition slightly more resistant to crevice attack at 37 °C. Therefore, it appears that the anomalously rough surface of the annealed condition does not markedly influence crevice corrosion. Grinding both the cold-worked and annealed conditions to a 120 grit finish (CW/120 and A/120), increases the percentage of crevice sites corroded.

Fig. 5 illustrates that electropolishing as the final surface preparation step significantly improves the resistance to crevice corrosion at both temperatures. Clearly, the advantages of electropolishing have a greater influence than the detrimental effect of a narrower crevice gap caused by the smoother surface of the electropolished surfaces. Whether electropolishing was applied to cold-worked or annealed samples, that were hand-buffed or vibratory polished had minimal influence on the subsequent resistance to crevice attack.

The beneficial affect of electropolishing only accrues when it is applied as the last surface modification operation. This is demonstrated by the severe crevice

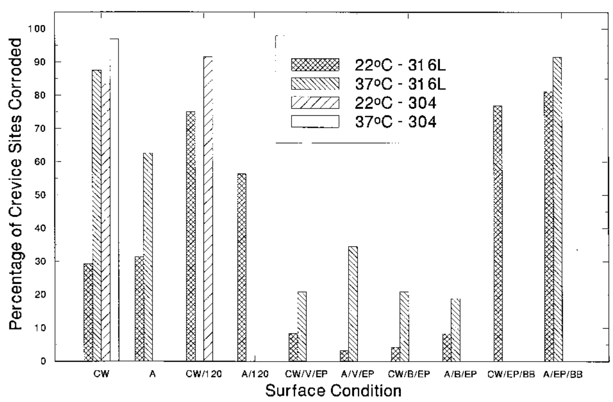

Figure 5 The percentage of crevice sites correded during the 72 h immersion in ferric chloride as a function of surface condition.

corrosion suffered by ''bead blasted'' surfaces that were previously electropolished (CW/EP/BB and A/EP/BB), which suffer crevice attack to a greater extent than surfaces ground to a 120 grit finish.

3.4. Pitting corrosion

Virtually no pitting occurred on the 25 × 50 mm surfaces of any samples. However, the transverse surfaces suffered pitting attack. As illustrated in Fig. 6, the most severe pitting occurred on the 'short transverse' surface – the 5.5 × 25 mm surface – which is normal to the rolling direction of the samples. Therefore, the susceptibility to pitting corrosion was determined by characterizing the pits on the short transverse surfaces, according to the average pit density and size. The pit density refers to the average number of pits per short transverse edge. For example the sample of Fig. 6a has seven pits. The pit size was rated on a five-point scale, with a rating of 1 if the surface diameter of the pit was $\lesssim$ 1 mm, a rating of 2 if the surface diameter was between 1 and 2 mm, and likewise to a rating of 5 corresponding to a pit surface diameter of $\gtrsim$ 4 mm. Fig. 6b illustrates pits rated according to this scale. Pits associated with crevice corrosion between the elastic bands and the sample edges were not included in the assessment of pitting.

Figs 7 and 8 summarize the severity of pitting corrosion for each sample condition. A notable result is that at 22 °C no pitting occurred on any of the cold-worked samples, regardless of the surface condition. Also for both test temperatures, comparison of the same surface preparation procedures reveals that annealed samples always exhibit a higher pit density. A striking example of this result is the comparison in Fig. 7 of the A/B/EP and CW/B/EP samples, both of which had the same surface preparation procedure, but the former has a much higher pitting density. The average pit size for the cold-worked and annealed conditions demonstrates a less pronounced trend. At 22 °C the average pit size of the annealed samples is always greater than the corresponding cold-worked sample (Fig. 8), but at 37 °C no distinct difference between the cold-worked and annealed conditions is evident.

A second important result, evident in Figs 7 and 8, is that surfaces for which bead blasting (BB) was the final finishing operation exhibit both a lower pit density and lower average pit size compared to samples for which electropolishing (EP) was the final finishing operation.

Similar to the result for crevice corrosion, Figs 7 and 8 demonstrate that whether electropolishing was applied to samples that were previously hand buffed or vibratory polished had a minimal influence on the pitting resistance.

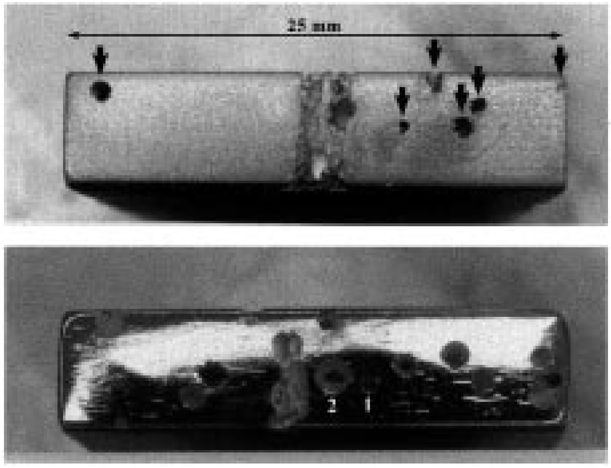

Figure 6 Photograph of transverse edges of samples after 72 h immersion in ferric chloride at 37 °C. Top: A/EP/BB surface preparation, arrows indicate pits included in pit density data. Bottom: A/V/EP surface preparation, numbers indicate pit size rating (see text).

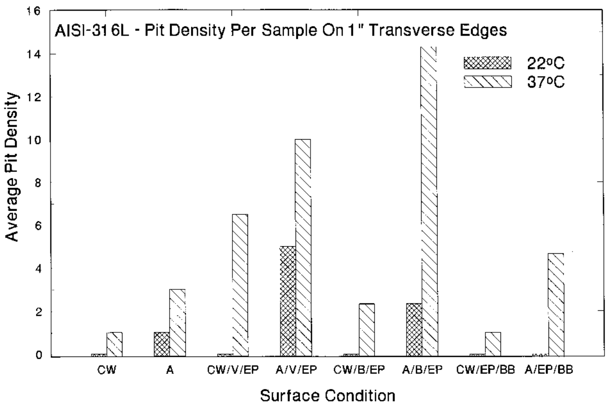

Figure 7 Pit density on transverse edges as a function of surface condition after 72 h immersion in ferric chloride.

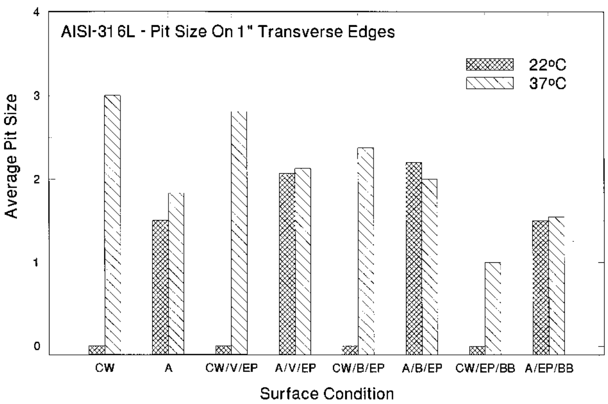

Figure 8 Pit size on transverse edges as a function of surface condition after 72 h immersion in ferric chloride.

4. Discussion

Because the 316L did not exhibit any evidence of general corrosion attack, the resistance to localized corrosion can be determined form weight loss measurements such as those illustrated in Fig. 4. However, whether the localized corrosion is due to pitting or crevice corrosion cannot be established from these weight loss measurements. Although ASTM G48 Method B is intended for the determination of the susceptibility to crevice corrosion, in the current reported tests both pitting and crevice corrosion occurred, and the separate contribution of these two mechanisms to the weight loss results of Fig. 4 cannot be individually determined. Therefore, weight loss measurements may not always provide a reliable indication of the susceptibility or resistance to crevice corrosion. From an applications viewpoint, the weight loss measurements may be a useful indicator of the quantity of metallic ions released from the implant into the surrounding tissue, but no information that can be used to improve the corrosion performance of the implant is generated.

A more rigorous examination of the ASTM G48, Method B test results allows separation of the crevice and pitting corrosion resistance. Based on the results of Fig. 5, it is clear that a final surface preparation step of electropolishing increases the resistance to crevice corrosion. Regardless of whether material was initially cold-worked or annealed, or whether surfaces were hand buffed or vibratory polished, the four conditions of Fig. 5 finished by electropolishing, exhibit a significantly lower percentage of sites at which crevice corrosion occurs. In contrast, the pit density results of Fig. 7 illustrate that when the final surface preparation step is electropolishing a much larger number of pits results. Furthermore, the pit size, according to Fig. 8, is comparable to the unprepared mill finished samples (CW or A), and considerably larger than the pitting attack on the samples finished by bead blasting (BB). Therefore, for the samples tested, there appears to be an inverse relationship between the susceptibility to crevice corrosion and pitting corrosion. This inverse relationship is somewhat anomalous since the initiation of pitting and crevice corrosion is often associated with non-metallic sulfide inclusions [7, 8]. Indeed, the observed higher density of pitting on the transverse surfaces has previously been suggested to be due to a larger number of exposed inclusion/matrix interfaces on these surfaces [14]. Despite the low sulfur content of Table I, the occurrence of pitting predominantly on the transverse surfaces suggests that inclusions play a role in the initiation of pitting in the current 316L.

In contrast to the results of the previous paragraph, the initiation of pitting and crevice corrosion has been suggested to occur via different mechanisms [15], with the initiation of crevice corrosion primarily influenced by the chemistry of the protective surface film, and pitting initiation influenced primarily by non-metallic inclusions. In the current work, since a protective surface film is left by electropolishing [1], this may account for the improved crevice corrosion resistance of samples for which the final surface preparation step was electropolishing (Fig. 5). However, for the samples bead blasted subsequent to electropolishing, the protective surface film associated with electropolishing would be eliminated during bead blasting, leading to the increased crevice corrosion. However, the reason for the greater susceptibility to pitting of the electropolished surfaces is unclear. As pitting corrosion is more closely associated with the presence of non-metallic inclusions, it may be speculated that the ''bead blasting'' procedure causes sufficient deformation of the matrix near the surface to embed the matrix/inclusion interface making it less prone to pitting attack.

The foregoing highlights that during the implant service life, it is important to know – for the particular application of interest – what type of localized attack occurs. During *in vivo* exposure, it is likely that both pitting and crevice corrosion will both occur. However, the current results indicate that the remedial action to minimize each mechanism may differ. Therefore, it must be determined which of the two mechanisms is responsible for the greatest release of metallic ions into surrounding tissue. Moreover, crevice corrosion may cause loosening of the implant, leading to further damage by fretting corrosion. Clearly, further research is required to delineate the influence of pitting, crevice and fretting corrosion as a function of surface condition. This is an objective of continuing research.

Contrary to previous results [2, 12], the results of Figs 7 and 8 indicate that the cold-worked state provides improved resistance to pitting corrosion. However, the composition of the cold-worked and annealed samples used in the current investigation were not the same (Table I). The most significant difference is the Mo content which was greater for the cold-worked material. Mo is known to significantly improve the resistance to localized corrosion of austenitic stainless steels [1, 16]. Therefore, from the current results it can not be determined whether the improved pitting resistance of the cold-worked condition is due to the metallurgical state or composition.

5. Summary and conclusions

1. Weight loss measurements generated from immersion tests, such as ASTM G48, may not be sufficient to determine the susceptibility to crevice corrosion independently from the susceptibility to other forms of localized corrosion.
2. The surface condition providing the best resistance to crevice corrosion may not provide the best resistance to pitting corrosion.
3. The best resistance to crevice corrosion is obtained when the surface is electropolished. Whether surfaces are previously mechanically polished by hand buffing or vibratory polishing has minimal influence on the crevice corrosion resistance following subsequent electropolishing.
4. The results indicate that for implant applications of 316L, the susceptibility to crevice, pitting and fretting corrosion must be independently assessed. Results characterizing the overall resistance to localized corrosion may not provide a true indication of the potential service performance.

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