Effect of Surface Treatment on the Surface Characteristics of AISI 316L Stainless Steel

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Abstract

The ability of 316L stainless steel to maintain biocompatibility, which is dependent upon the surface characteristics, is critical to its effectiveness as an implant material. The surfaces of mechanically polished (MP), electropolished (EP) and plasma treated 316L stainless steel coupons were characterized by X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES) for chemical composition, Atomic Force Microscopy for surface roughness, and contact angle measurements for critical surface tension. All surfaces had a Ni concentration that was significantly lower than the bulk concentration of ~13%. The Cr content of the surface was increased significantly by electropolishing. The surface roughness was also improved significantly by electropolishing. Plasma treatment had the reverse effect – the surface Cr content was decreased. It was also found that the Cr and Fe in the surface exist in both the oxide and hydroxide states, with the ratios varying according to surface treatment.

Introduction

Stents, fracture fixation plates and screws, spinal implant devices, aneurysm clips, intramedullary nails and pins, temporary fixation devices, and surgical instruments, among others, have been manufactured from AISI 316L stainless steel for several years. While the mechanical performance of implants and devices may be governed by bulk properties, interaction with the environment is governed by the characteristics of the surface layer. In the case of biomedical devices two interactions that are of paramount importance are corrosion resistance (which is related to leach rates) and biocompatibility.

The performance of the surface layer is in turn dependent on a number of its characteristics or features. These include its detailed chemical composition, thickness, microporosity, surface charge states, surface roughness, total surface area (as opposed to geometric area), and critical surface tension, among others. These characteristics are highly processing dependent. The chemical composition, for instance, can be significantly different from that of the bulk. The specific process employed to alter the surface plays a major role in determining its properties. Two processes that are widely employed with stainless steels, for surface modification, are electropolishing and passivation.

Surface Characteristics, Corrosion and Biocompatibility

The effect of surface characteristics and surface treatments on the corrosion resistance and biocompatibility of AISI 316L stainless steel has been researched by several investigators in the past. Bordji and co-workers[1] investigated the effect of glow discharge nitrogen implantation, carbon-doped stainless steel coating sputtering and low temperature plasma nitriding on the biocompatibility of 316L stainless steel, as studied with human osteoblast and fibroblast cultures. They found the first two treatments resulted in biocompatible surfaces whereas the plasma nitrided surface resulted in dramatic cellular interactions. The effect of different passivation techniques on the *in vitro* corrosion resistance of 316L wires was studied by Shih et al.[2] Only amorphous oxidation was found to improve the corrosion resistance of the alloy. The improvement was attributed to the removal of the plastically deformed native oxide layer and the replacement with a newly grown, more uniform and compact oxide layer composed of nano-scale oxide particles with higher oxygen and chromium concentrations. The authors reported that the properties of the surface oxide layer, rather than its thickness, seem to be the predominant factor in the improvement of *in vitro* corrosion

resistance. Changes to the wettability characteristics of 316L stainless steels by Nd:YAG laser treatment and its effects on the cell response of human fibroblast cells was studied by Lawrence et al.[3] The wettability characteristics of the 316L were found to improve and were attributed to modifications to the surface roughness, changes in the surface oxygen content and the increase in the polar component of the surface energy. Cell proliferation and adhesion on the laser treated 316L were found to be consistently less than on the untreated samples. The authors state that this effect is due entirely to the increased surface roughness affected by the laser treatment. The interaction of human cardiac artery endothelial cells with 316L stainless steel, with varying degrees of surface roughness, was evaluated by Rohly and co-workers.[4] They found that cell growth was promoted by the overall smoother surface of the control specimens over that of the specimens that had 60 ~ 240 grit surfaces.

The relationship of the critical surface tension of a solid surface to its biocompatibility was reported by Baier.[5] Based on Baier's work, a surface is biocompatible when its critical surface tension is between 20×10^{-3} N/m and 30×10^{-3} N/m. Selvaduray and Bueno studied the effect of plastic strain in combination with electropolishing and passivation on the critical surface tension of 316L.[6] They found that the surface treatment consisting of electropolishing, followed by passivation for 30 minutes in 30% nitric acid resulted in a surface which had a critical surface tension between $20 \sim 30 \times 10^{-3}$ N/m. It was also reported that surface plastic strains of up to 30% did not result in a significant change to the critical surface tension.

The relationship between surface charge and cellular adhesion was investigated by measuring the adhesion strength over a range of charge densities.[7] The cells were found to show charge and electrical potential-dependent adhesion maxima, suggesting that surface alloying for optimum adherence would be a possibility.

Trigwell & Selvaduray found that the composition of the surface oxide layer, rather than the surface roughness or surface area, was more important in determining the corrosion rate of NiTi alloys that had been mechanically polished, electropolished, chemically etched and plasma etched.[8]

Electropolishing is an electrochemical process that involves removal of material from the specimen being "polished", in an electrolyte, with the specimen as the anode. The electrolyte is usually a H_3PO_4-H_2SO_4 solution. Direct current is employed to effect the material removal. It is reported that electropolishing selectively removes material from the high points at a rate faster than material removal from the depressions or "valleys", resulting in a smoother surface and thus achieving the polishing effect.[9] During this process a film also forms on the surface of the object being electropolished.

One of the issues when dealing with materials for biomedical applications is the residual concentration of microbes and other biological agents. Changing the surface functional groups of materials can change the bacterial adhesion, depending upon the surface hydrophobicity.[10] Boyd et al. found that an increase in the surface roughness of stainless steel surfaces increased bacterial adhesion.[11] Therefore there is concern about the effectiveness of surface treatments in deleting biological contaminants. Plasma treatment can potentially be effective in removing biological contamination.

There has been a significant amount of work devoted to studying the effects of various surface treatments on biocompatibility, as measured or evaluated by different means, including in vitro studies. Research that has attempted to characterize in detail the manner in which surface treatments affect the surface chemistry, morphology and thermodynamic stability, and how these in turn may affect biocompatibility and corrosion behavior of implants has not been that extensive. There is a need to study these relationships so that a broader understanding of the factors that affect the biocompatibility of implants can be developed.

The overall purpose of this study is to investigate the effect of surface treatment on the surface characteristics and surface chemistry of NiTi, Co-Cr and AISI 316L metallic alloys so that their corrosion characteristics and biocompatibility behavior can be better understood and correlated. The results reported in this paper represent the first phase of the study, which focused on AISI 316L stainless steel. The effects of mechanical polishing, electropolishing, and each of these with subsequent plasma treatment, on the surface roughness, surface chemistry, and critical surface tension of 316L stainless steel were studied.

Experimental Procedure

The AISI 316L coupons used for this investigation were 19 mm x 19 mm x 0.737 mm thick. The results of the independent chemical analysis that was done to verify that the chemical composition was withing specifications are shown in Table 1.

Three surface treatments were employed: mechanical polishing, electropolishing, and mechanical and electropolishing each followed by plasma treatment. Prior to any surface treatment, the specimens were first cleaned with alkanox in deionized water at 70°C followed by immersion in an ultrasonic cleaner for 1 minute, followed by rinsing in 1 liter of deionized water for 30 seconds. If a water break occurred, the alkanox cleaning step was repeated. The specimens were rinsed one more time in 1 liter of deionized water, at 80°C, for 30 seconds.

The mechanically polished specimens had their surfaces ground with 1000 grit SiC paper and water to produce a

uniform scratch pattern on the surface. The specimens were cleaned again following mechanical polishing.

Table 1: Chemical composition of 316L stainless steel

Element	Actual		Specification
	Wt %	At %	
C	0.02	0.09	< 0.030
Mn	1.92	1.95	< 2.00
P	0.022	0.04	< 0.045
S	0.002	~ 0	< 0.030
Si	0.29	0.58	< 1.00
Cr	17.54	18.86	16.00 ~ 18.00
Ni	13.78	13.12	10.00 ~ 14.00
Mo	2.76	1.61	2.00 ~ 3.00
Cu	0.09	0.08	NS*
Fe	Balance	63.66	Balance

* Not Specified

For electropolishing the specimens were first mechanically polished, as described above. They were then activated in a 50% concentrated H_2SO_4 solution at 70°C for 1 minute. The electropolishing solution used was 63% H_3PO_4, 15% H_2SO_4 and 22% deionized water, and maintained at 55°C ± 5°C. The current density was ~ 12.9 x 10^2 A/m² and electropolishing was done until the scratches from the mechanical polishing were removed and a mirror finish obtained. After electropolishing the specimens were rinsed in deionized water, dried, and the surfaces examined in a SEM to ensure uniform polishing.

Mechanically and electropolished specimens were also subjected to atmospheric plasma glow discharge (APGD) treatment. The advantage of APGD is that it is low temperature (minimizing thermal damage) and can be performed in air without the need for a vacuum chamber. The specimens were exposed to a 98 % He-2 % O_2 RF plasma at 300W for 5 minutes with a Surfx Technologies Atomflo 1500R plasma source.

The surfaces of the mechanically polished and electropolished specimens, before and after plasma treatment, were analyzed by Auger electron spectroscopy (AES) using a Phi-5600 instrument and X-ray photoelectron spectroscopy (XPS) which was a Kratos XSAM 800. Contact angles were measured on an AST Products VCA Optima instrument equipped with an environmental chamber set at 37 °C. The critical surface tension was determined following the method of Zisman.[12,13]

The surface roughness was measured with a Nanosurf E-AFM atomic force microscope. Ten area scans were taken on each specimen. The scanned area each time was 10 μm by 10 μm.

Surface Roughness

The average surface roughness of the specimens that were mechanically polished (MP), electropolished (EP), and before and after plasma treatment, is shown in Table 2. Electropolishing was effective in reducing the surface roughness significantly, down to less than half the surface roughness after mechanical polishing, with an improvement in the uniformity of the surface as well, as evidenced by the decrease in the standard deviation. Plasma treatment had no observable effect on the surface roughness, within the experimental parameters.

Table 2: Effect of electropolishing on surface roughness

	MP	EP	EP+ Plasma	MP+ Plasma
Roughness Average (Å)	32.15	14.66	14.06	29.83
Standard deviation (Å)	8.03	3.60	5.23	8.82

X-ray Photoelectron Spectroscopy

The high resolution XPS data for the C, O, Cr, and Fe peaks are summarized in Table 3. This information was used to deduce the changes in surface chemistry that occur as a result of the surface treatments employed.

Electropolishing: When mechanically polished specimens were electropolished, the characteristics of the oxygen bonds changed. There was a drop in oxygen bonding in the oxide form and a dramatic increase in oxygen bonding as a hydroxide. The chemical composition of the chromium on the surface also changed with electropolishing. In the mechanically polished specimen Cr was bound primarily in the oxide form (Cr_2O_3). After electropolishing, the proportion of Cr in the hydroxide form increased significantly, though the majority of the chromium was still bound as an oxide. Electropolishing also caused a change in the binding of the iron on the surface. There was a decrease in metallic iron, and an increase in Fe bound as FeO, which is adherent to steel substrates. This was offset by a drop in Fe bound as Fe_2O_3 and the hydroxide. However, more than 50% of the Fe is still bound as Fe_2O_3.

The Cr:Fe ratio, which is 1:3.63 in the bulk alloy dropped to 1:1.71, leading to an "enrichment" of chromium on the surface when 316L is electropolished. It must be pointed out that the Cr:Fe ratio for the mechanically polished specimens also indicates surface enrichment of Cr, as compared to the bulk, probably due to preferential atmospheric oxidation of the chromium. However, the data in Table 3 indicate that electropolishing can result in further enrichment of chromium oxide on the surface.

Table 3: Relative chemical composition (atomic percent) of surfaces by XPS

	Bond Type	MP	EP	EP+ Plasma	MP+ Plasma
Carbon	C-C/C-H	72.2	71.6	74.7	77.1
	C-O	15.5	16.2	14.8	12.4
	C=O	5.9	5.3	3.9	4.5
	COO-	5.9	5.1	3.9	3.7
	O-C=O	0.5	1.7	2.7	2.4
Oxygen	O=	59.9	11.9	27.2	65.1
	O-H	32.1	70.0	59.7	28.1
	O(H$_2$O)	8.0	18.1	13.1	6.8
Chromium	Cr	13.0	16.3	11.2	7.9
	Cr$_2$O$_3$	67.3	48.4	68.9	80.1
	Cr-OH	19.7	35.3	19.9	12.1
Iron	Fe	9.4	5.6	5.1	0.6
	FeO	9.6	16.3	4.5	0.7
	Fe$_2$O$_3$	59.8	51.5	76.0	81.7
	Fe-OOH	17.4	12.1	10.7	15.7
	Fe Sat	3.8	14.6	3.7	1.3
Cr:Fe Ratio		1:2.10	1:1.71	1:1.82	1:5.88

Plasma Treatment: The effect of plasma treatment, regardless of whether the specimens were mechanically polished or electropolished, was relatively consistent. The proportion of oxygen bound in the oxide form increased in the plasma treated specimens, with a slight drop in the proportion bound as a hydroxide. This is consistent with the finding that the proportion of Cr as Cr$_2$O$_3$ and Fe as Fe$_2$O$_3$ were both found to increase appreciably, with corresponding drops in metallic Cr and Fe, and chromium and iron hydroxides. It should be noted that Fe bound in the form of FeO also dropped dramatically, leading to the conclusion that the plasma treatment used in this investigation had the effect of oxidizing divalent Fe.

The Cr:Fe ratios indicate a dramatic drop in the chromium concentration of mechanically polished specimens when they are plasma treated – from 1:2.10 to 1:5.88. Plasma treating electropolished specimens also reduced the Cr:Fe ratio, though to a far lesser extent. Electropolishing appears to significantly reduce the "chromium-depleting" effect of plasma treatment.

Significant amounts of P, S, and Ca were detected on the EP surfaces; these are thought to be residues from the electropolishing process. Most of this residual contamination was removed by the plasma treatment.

Auger Electron Spectroscopy

The chemical composition and thickness of the surface oxide layer as determined by Auger Electron Spectroscopy (AES)

are summarized in Table 4, and one depth profile - for the electropolished specimen - is shown in Figure 1.

Table 4: Relative chemical composition (atomic percent) and oxide layer thickness of surfaces by AES

Element	MP	EP	EP+ Plasma	MP+ Plasma
O	63	66	69	70
Cr	16	20	10	10
Fe	18	10	16	18
Ni	3	3	5	2
Thickness	~ 40 Å	~ 35 Å	~ 35 Å	~ 75 Å

Electropolishing: It can be seen from the data in Table 4 that electropolishing is effective in enhancing the Cr content of the surface oxide layer, along with a reduction in the Fe content. This becomes clear when the Cr and Fe concentrations in the mechanically polished and electropolished specimens are compared. It is rather interesting to note that the Ni content is significantly lower than the bulk composition of 13.78 % in all the specimens; electropolishing did not affect the Ni concentration. Electropolishing also does not change the thickness of the surface oxide layer significantly.
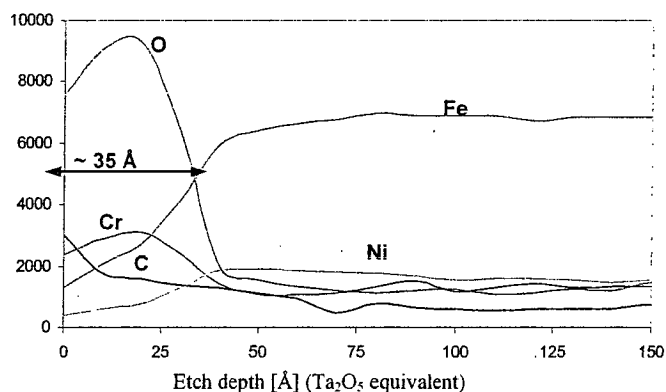

Figure 1: AES depth profile of electropolished 316L stainless steel

Plasma Treatment: Treating the surface with a plasma has the reverse effect of electropolishing. The Cr content decreases and the Fe content increases. Plasma treatment of the mechanically polished specimens resulted in a noticeable increase in the oxide layer thickness, probably due to oxidation of the FeO to Fe$_2$O$_3$. Again, as was deduced from the XPS data, electropolishing the specimens first, prior to plasma treatment, prevented this change in the surface oxide layer thickness. The Ni content does not appear to be affected significantly.

Critical Surface Tension

The critical surface tension values measured at 23°C are summarized in Table 5. The Zisman plot for one condition – the mechanically polished specimens at 23°C – is shown in Figure 2. The data indicate that plasma treatment increases the thermodynamic stability of the surfaces, which can be seen by inspecting the data at 23°C. This is consistent with the XPS data that show an increase in the Cr_2O_3 and Fe_2O_3 concentrations following plasma treatment. These compounds are also thermodynamically more stable than the other Fe and Cr compounds.

The decrease in the critical surface tension following electropolishing can be attributed to the decrease in the Cr_2O_3 and Fe_2O_3 concentrations, coupled with an increase in the Dr, Cr-OH and FeO concentrations, all of which are thermodynamically less stable than Cr_2O_3 and Fe_2O_3.

Table 5: Critical surface tension as a function of surface treatment

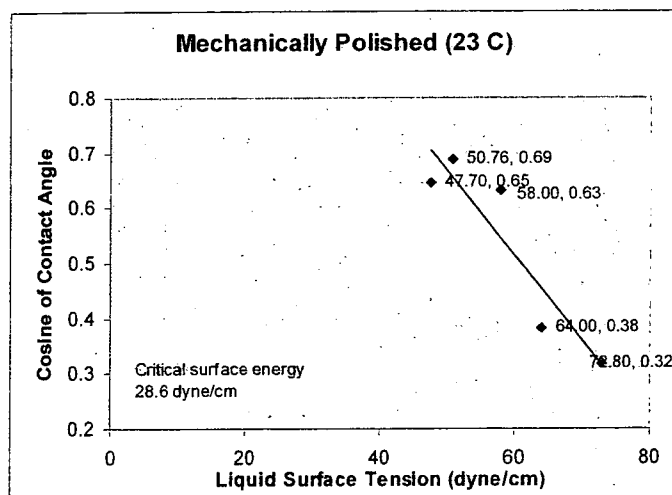| Temp	23°C
MP	28.6
EP	21.0
EP+Plasma	27.5
MP+Plasma	33.0
PTFE	15.6

Figure 2: Zisman plot for mechanically polished specimen, at 23°C.

Discussion of Results

The results obtained from AES and XPS are consistent with one another, namely that electropolishing enriches the Cr concentration in the surface oxide layer. The fact that electropolishing is done in an aqueous environment is most probably the cause for the increase in the chromium hydroxide content.

The surfaces of the 316L stainless steel specimens tested are not composed entirely of Cr_2O_3; they are really "mixed oxides" and "mixed hydroxides", containing primarily both chromium and iron oxides and hydroxides. This is consistent with the findings reported by others that the surface oxide passivation layer on ferrous alloys is a complex mix of oxides, hydroxides and oxyhydroxides.[14] Electropolishing of mechanically polished specimens was found to increase the chromium hydroxide content on the surface. Further analysis is necessary to determine the exact composition. It also resulted in the FeO concentration increasing and the Fe, Fe2O3 and Fe-OOH concentrations decreasing.

Despite there being 13.78 % Ni in the bulk of the alloy itself, the surface contains only about 3 %, even for the specimens that were mechanically polished. For biomedical applications this can be a desirable finding as nickel has been known to cause allergic reactions in some individuals.

Plasma treatment was found not to enhance the surface passivation, but reduced the Cr:Fe ratio. When the XPS and AES data are interpreted in combination, plasma treatment of the surfaces increases the concentration of Cr in the oxide form, as opposed to the hydroxide form. It also resulted in an increase of Fe in the Fe_2O_3 form. This combined effect resulted in an increase in the critical surface tension of the plasma treated specimens, signifying an increase in the thermodynamic stability of the surfaces.

While the surface might be constituted of thermodynamically more stable species, the extent to which this layer is able to isolate the bulk from the host environment is also heavily dependent on its microstructure. Less adherent and porous surface layers can provide little protection regardless of thermodynamic stability.

The potential benefit of the plasma treatment is that it removed residual contamination from the electropolishing process. Work is in progress to further evaluate the effectiveness of plasma treatment in removing contamination from 316L surfaces, with different gases. This effort will also study the effect of plasma treatment in enhancing surface passivation.

Conclusions

Regardless of the surface treatment, it was found that the surface oxide layer on 316L stainless steel contains

significantly less Ni as compared to the bulk composition. Electropolishing was found to be effective in enriching the Cr content of the surface. However, the surface layer is not entirely Cr_2O_3. It contains both Cr and Fe oxides and hydroxides. The type of surface treatment affects the relative ratios of these constituents. Electropolishing results in a smoother surface. Plasma treatment, while it can have the potential benefit of eliminating biological contamination, was found to affect the surface chemistry in a deleterious manner by causing the Cr concentration to decrease.

Acknowledgements

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