

Effects of Surface Treatment on Corrosion Resistance of 304L and 316L Stainless Steel Implants in Hank's Solution

Saeid Ghanavati¹, Mohammad Reza Shishesaz^{2*}, Mansoor Farzam², and Iman Danaee²

¹M.S.Student, Department of Technical Inspection Engineering, Petroleum University of Technology, Abadan, Iran

²Associate Professor, Department of Technical Inspection Engineering, Petroleum University of Technology, Abadan, Iran

Received: December 04, 2013; *revised:* November 18, 2014; *accepted:* January 01, 2015

Abstract

The enormous demands for metal implant have given rise to a search for cheap material with good bio-tolerability and resistance to corrosion. Although stainless steel has these properties and is widely used for this purpose, its long term application is still a concern. The corrosion resistance of stainless steel depends on the passive layer. Herein, chemical surface treatment, including passivation, electropolishing, and acid cleaning is used for improving the corrosion-resistance property of AISI 316L and 304L. Cyclic polarization, electrochemical impedance spectroscopy, and EDX analysis were used to investigate the properties obtained thereby. Finally, the corrosion resistance of the untreated and modified specimens was compared. The results show that the corrosion behavior of the passivated and electropolished specimens is improved.

Keywords: Chemical Passivation, Impedance, Corrosion, Electropolishing

1. Introduction

Metals and alloys have a wide application in dentistry, medicine, orthopedic, and bone fractures as a component of an artificial implant or restored materials. Recently, alloys that are being used as implants are titanium alloys, austenitic stainless steel, and chromium-cobalt alloys. The advantages of stainless steels compared with other materials are its mechanical property, low cost, the ease of fabrication, and acceptable corrosion resistance. Many applications of metals and alloys are for the structural implant; therefore, metal biocompatibility is important, since metals can be corroded in bio-environments. In fact, biocompatibility means that the tissue of the person using implant materials does not suffer from any irritating, toxic, allergic, inflammatory, mutagenic, or carcinogenic action (Sharan, 1999 and Shih et al., 2004). The implant corrosion causes adverse effects on the implant itself and on the surrounding tissues. Corrosion deteriorates the mechanical properties of the implant and produces chemical species which are harmful for human organs. Therefore, the corrosion resistance of a metallic implant is an important aspect of its biocompatibility, even though metals, without considering the biocompatibility requirement, are certainly proposed for temporary implants (Hermawan et al., 2010). Stainless steels have high corrosion resistance due to the presence of a thin

* Corresponding Author:
Email: shishesaz@put.ac.ir

passive film on the surface. Although these passive films have typically a thickness of only a few nanometers, they show a high protective barrier between the aggressive biological environment and the metal surface. Consequently, the passive film kinetically retards the dissolution rate of metals by many orders of magnitude. The properties of this passive film are effectively dependent on the alloy composition, but can also largely be influenced by chemical finishing and mechanical processes. These finishing treatments are made after producing the material in the steel mills and/or after further processing into the final products (Hofmann et al., 2006; Ladwein et al., 2004; Burkert et al., 2004). Therefore, for overcoming the corrosion reactions following the use of implants in the human body and increasing the life time of these materials after implantation, the surface treatment of metals is often required. Surface treatments like acid dipping, ultrasonic cleaning, thermal treatment, electrochemical and mechanical polishing, plasma exposure, and laser surface melting are the most commonly used surface treatment methods (Wu et al., 2008; Zhao et al., 2002; Haidopoulos et al., 2006; Baron et al., 2006).

In the present research, the effects of some of these surface treatments including mechanical polishing, acid cleaning, chemical passivation, and electropolishing are studied.

2. Materials and methods

2.1. Materials

Austenitic stainless steels were purchased from AISI 316L with the chemical composition of C=0.028%, Cr=16.75%, Ni=10.15%, Mo=2%, and Fe balance. Also, AISI 304L with the weight composition of C=0.017%, Cr=18.32%, Ni=8.03%, Mo=0.29% and Fe balance was used. The electrochemical experiments were carried out in the simulated physiological Hank's solution composed of 8 g^l⁻¹ NaCl, 0.40 g^l⁻¹ KCl, 0.35 g^l⁻¹ NaHCO₃, 0.25 g^l⁻¹ NaH₂PO₄·2H₂O, 0.06 g^l⁻¹ Na₂HPO₄·2H₂O, 0.19 g^l⁻¹ CaCl₂·2H₂O, 0.41 g^l⁻¹ MgCl₂·6H₂O, 0.06 g^l⁻¹ MgSO₄·7H₂O, and 1 g^l⁻¹ glucose. All the chemical materials were purchased from Merck chemical Co. (Darmstadt, Germany) and were used as received without further purification. The specimen had a dimension of 20 mm in diameter and 4 mm in thickness. All the samples were ground with emery paper down to 2000 mesh and mechanically polished, which were then code-named MP; one sample was subjected to chemical passivation, another one was subjected to acid cleaning, and the other sample was subjected to electropolishing for passivation. After each treatment, the specimens were rinsed with distilled water.

2.2. Surface treatment process of electro polishing

Specimens were electropolished in an electrolyte solution composed of sulfuric acid (50 v/v%) and orthophosphoric acid (50 v/v%) with the current density of 15 amp/dm² at 75 °C for 3 minutes and were then code-named EP.

2.3. Surface treatment process of chemical passivation

The specimens were passivated in 30 vol.% HNO₃ solution for 20 minutes at 60 °C according to ASTM A967 and were then code-named CP.

2.4. Surface treatment process of acid cleaning

Acid cleaning was carried out according to ASTM A380 in a solution containing 25 vol.% HNO₃ and 8 vol.% HF at room temperature and then in a solution containing KMnO₄ and NaOH. These specimen were code-named AC.

2.5. Electrochemical analysis

The corrosion resistance property of all the surface-treated specimens in comparison to the non-treated specimens was investigated by electrochemical analysis. The exposed surface of the samples is 1 cm². The scan rate was adjusted to 1 mVs⁻¹ using an Auto Lab potentiostat with an Ag/AgCl reference electrode and platinum as the counter electrode. In order to stabilize the potential at OCP, before starting polarization tests, the specimens were immersed in hank's solution for 25 minutes. Electrochemical impedance spectroscopy was also carried out using this device. The data analysis was carried out using GPES and FRA software from Auto Lab Model PGSTAT 302N Potentiostat. The EDX analysis was also performed to evaluate the surface composition.

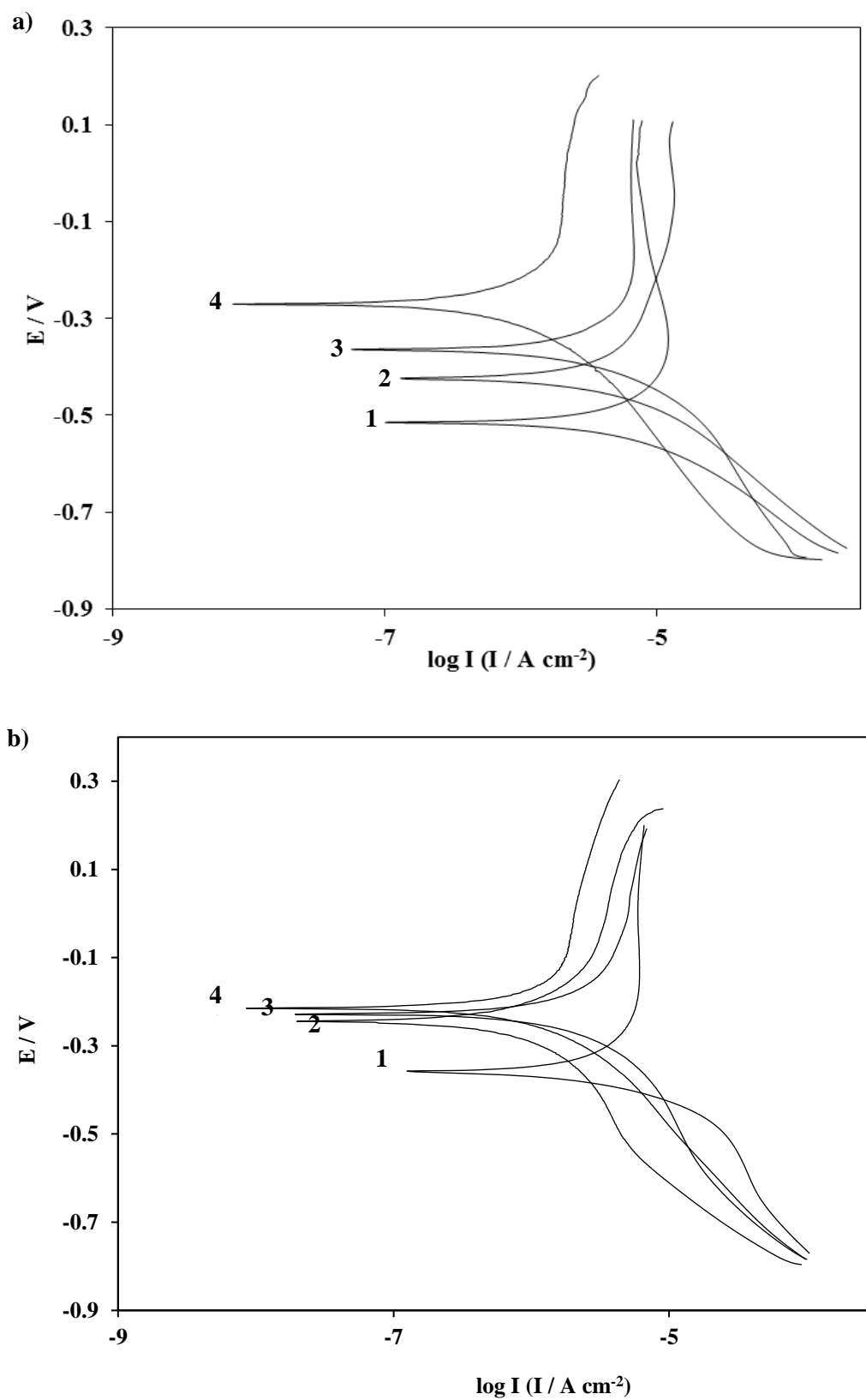
3. Results and discussion

3.1. Corrosion resistance

Figure 1 shows the normal cyclic polarization curves of stainless steel AISI 304L and 316L with different surface treatments in the test solution. It is obvious that all the chemical treatments improve the corrosion property of the samples, but at different levels. The mean value of corrosion potential and current densities were obtained by Tafel extrapolation method and are given in Table 1. From Table 1 and Figure 1, it is clear that chemical passivation in nitric acid has a considerable effect on the corrosion resistance of these stainless steels and leads to the lowest current density and nobler potential (-0.215 in case of 316L and -0.282 in case of 304L). Moreover, the electrochemical polishing for passivation has the best result after it. In the case of AISI 304L, acid cleaning shows the lowest corrosion resistant properties after mechanical polishing and the same trend occurs in sample AISI 316L. Improvements in corrosion resistant properties probably are due to several factors such as the change in surface composition, roughness, and surrounding environment. The pitting potential of the passivated and electropolished samples was also increased, which was attributed to an increase in Cr and Mo content and the removal of MnS inclusions. The obtained results are in agreement with other literatures (Ahmadian et al., 2013; Lee et al., 2003; Ziemniak et al., 2008).

Table 1
Results of electrochemical corrosion test in Hank's solution for (a) 304L and (b) 316L.

a)	Surface treatment	$I_{corr.}(A/cm^2)$	$E_{corr.}(V)$	B_a (V/dec)	B_c (V/dec)	R_p (ohm)	E_p (V)	$E_{pit}-E_{pro}$
	MP	5.98E-07	-3.59E-01	0.203	0.096	79842.1405	0.352	5.10E-02
	AC	2.14E-07	-2.48E-01	0.173	0.134	168837.627	0.258	3.66E-01
	CP	1.84E-07	-2.15E-01	0.195	0.131	355237.255	0.342	4.15E-01
	EP	1.98E-07	-2.28E-01	0.163	0.182	343208.49	0.228	2.19E-01
b)	Surface treatment	$I_{corr.}(A/cm^2)$	$E_{corr.}(V)$	B_a (V/dec)	B_c (V/dec)	R_p (ohm)	E_p (V)	$E_{pit}-E_{pro}$
	MP	1.10E-06	-3.65E-01	0.114	0.170	45420.6424	0.190	3.78E-01
	AC	8.14E-07	-4.24E-01	0.109	0.203	63875.0351	0.133	1.13E-01
	CP	1.02E-07	-2.82E-01	0.184	0.101	468993.633	0.376	1.99E-01
	EP	5.79E-07	-5.15E-01	0.178	0.111	86510.2742	0.120	8.70E-02

**Figure 1**

Cyclic polarization curves for the neat and chemically treated specimens; (a) 304L and (b) 316L; 1, 2, 3, and 4 correspond to MP, AC, EP, and CP respectively.

3.2. EDX analysis

The surface composition of the samples changes during the surface treatment. These changes include the formation of a surface passive layer that can increase the corrosion resistance of the alloys. The corrosion resistance of stainless steels is mainly due to the high protective quality of hydrated chromium oxy-hydroxide, which depends on the total amount of chromium in the surface film formed by different surface treatment (Linden et al., 2000 and Hashimoto et al., 2007). Table 2 show the chromium content after different surface treatments; as shown in this table, chromium enrichment occurs during chemical passivation and electropolishing and this enrichment is higher in the first case. The chromium enrichment in chemical passivation is due to nitric acid, which is a strong oxidizing agent and, in the case of electropolishing, it is due to the capability of this process for selective dissolution leading to the formation of a passive layer. Increasing Cr/Fe ratio after this process increases the corrosion resistance (Haidopulos et al., 2005; Okado et al., 2008; Grubb et al., 2004; Hashimoto et al., 2007). It is well known that hydrofluoric acid is a weak but extremely corrosive agent; as one can notice from the results obtained, when this acid is mixed with nitric acid, it reduces Cr content and thereby decreasing the corrosion resistance of stainless steel. In addition, increasing the corrosion resistance of stainless steels is ascribed to improving the thickness and compaction of the oxide layer in the surface treatment process.

Table 2

Chromium content after different surface treatments in (a) 304L and (b) 316L.

	Surface treatment	MP	CP	AC	EP
a)	Cr content	18.45	18.97	17.57	18.78
b)	Cr content	16.67	17.39	16.88	17.01

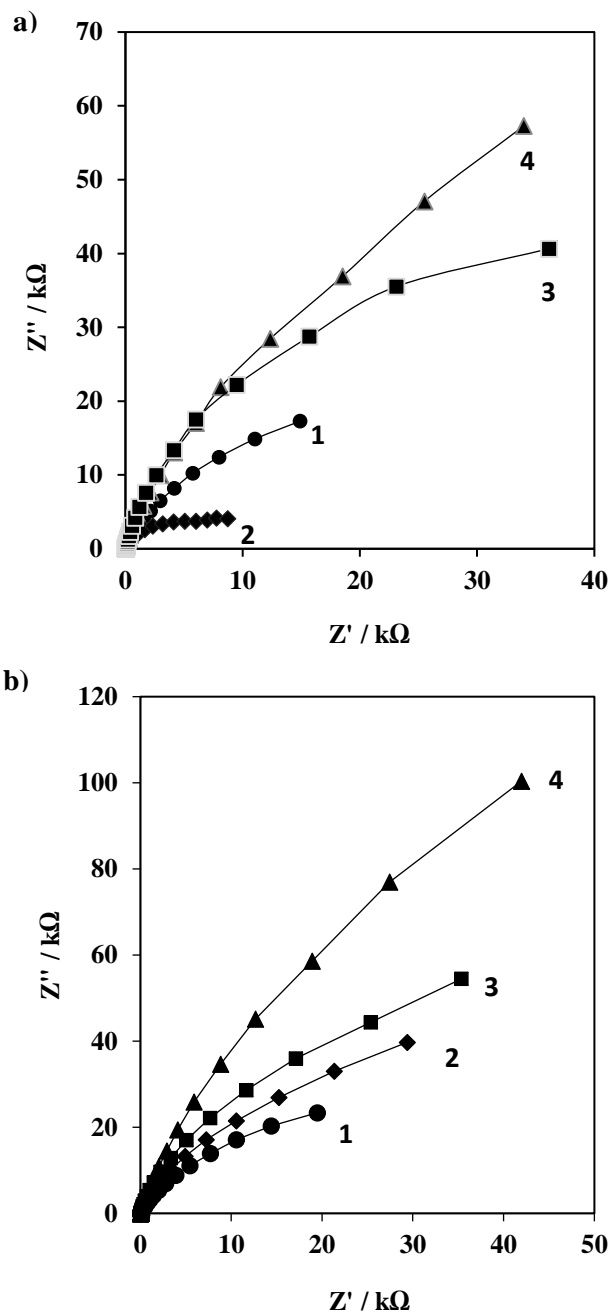
3.3. Impedance measurement

The results of impedance measurement show a visible dependence of electrochemical property on the treatment. The EIS spectra of the tested samples are shown in Figure 2. The increase in the semi-circle arc indicates an increase in the passive film stability and a decrease in that radius denotes a decrease in the passive film resistance (Ningshen et al., 2011). Because the obtained impedance spectra are relatively simple, they were modeled by a simple parallel combination of resistor and capacitor in series with a resistor (uncompensated solution resistance); this equivalent circuit is shown in Figure 3. Moreover, the passive layer resistance was determined. Table 3 shows the passive layer resistance of different chemical treatments, which confirms the polarization curve shown in the previous section. In the case of 304L, R_2 increases relatively in the order of CP>EP>MP>AC, revealing that the passive film presents a higher resistance to charge transfer process, which can be associated with the highest content of chromium in the film (Freire et al., 2010; Wallinder et al., 2000).

Table 3

Passive layer resistance for the neat and chemically treated specimens in Hank's solution: 304L and 316L.

Surface treatment	R_2 (304L) (ohm)	R_2 (316L) (ohm)
MP	4.96E+4	6.24E+4
AC	9.90E+3	9.32E+4
CP	1.50E+5	3.52E+5
EP	9.30E+4	1.34E+5

**Figure 2**

EIS plot for the neat and chemically treated specimens in Hank's solution; (a) 304L and (b) 316L; 1, 2, 3, and 4 correspond to MP, AC, EP, and CP respectively.

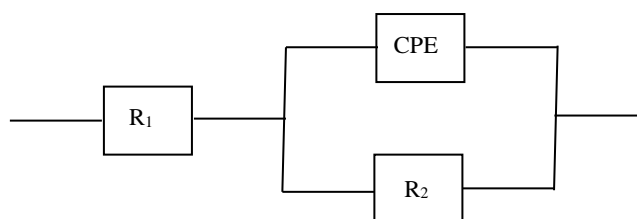


Figure 3
Equivalent circuit model.

4. Conclusions

The effects of surface treatments such as electropolishing, chemical passivation, acid cleaning, and mechanical polishing on the corrosion resistance of stainless steel 316L and 304L were investigated by electrochemical polarization, impedance spectroscopy, and surface analysis. The electrochemical tests showed that the chemical passivation and electropolishing of both types of stainless steels improved corrosion resistance and pitting potential, which was ascribed to chromium and molybdenum enrichment and MnS inclusion removal; this also makes it more reliable for applications in human body. Finally, the enhancement of corrosion resistance is due to the improvement in the thickness and compaction of the oxide layer.

Nomenclature

CPE	: Constant phase element
E_{corr}	: Corrosion potential
E_{pro}	: Protection potential
E_{pitt}	: Pitting potential
i_{corr}	: Corrosion current density
R_{ct}	: Charge transfer resistance
R_p	: Polarization resistance
R_s	: Solution resistance

References

- Ahmadian, Z., Danaee, I., and Golozar, M. A., Effects of Surface Treatment on Corrosion Resistance of 316 Stainless Steel Implants in Tyrode Solution, *Materials Testing*, Vol. 55, p. 294-299, 2013.
- Baron, A., Simka, W., Nawrat, G., and Szewieczek, D., Influence of Electrolytic Polishing on Electrochemical Behavior of Austenitic Steel, *Achievements in Materials and Manufacturing Engineering*, Vol. 18, p. 55-58, 2006.
- Burkert, A., Schilling, K., and Heyn, A., The Influence of Grinding Treatment of Stainless Steels on the Corrosion Behavior, *Materials and Corrosion*, Vol. 55, No. 10, p. 787-793, 2004.
- Freire, L., Carmezim, M. J., Ferreira, M. G. S., and Montemor, M. F., The Passive Behavior of AISI 316 in Alkaline Media and the Effect of pH: A Combined Electrochemical and Analytical Study, *Electrochimica Acta*, Vol. 55, No. 21, p. 6174-6181, 2010.
- Grubb, J. F., Fritz, J. D., and Polinski, R. E., Surface Treatment to Improve Corrosion Resistance of Austenitic Stainless Steels, United States Patent, No. US 6709528, 2004.

- Haidopoulos, M., Bournet, C., Turgeon, S., Laroche, G., and Mantovani, D., Development of an Optimized Electrochemical Process for Subsequent Coating of 316 Stainless Steel for Stent Applications, *Materials Science: Materials in Medicine*, Vol. 17, No. 7, p. 647-657, 2006.
- Haidopoulos, M., Turgeon, S., Laroche, G., and Mantovani, D., Surface Modifications of 316 Stainless Steel for the Improvement of its Interface Properties with RFGD-deposited Fluorocarbon Coating, *Surface and Coatings Technology*, Vol. 197, No. 2, p. 278-287, 2005.
- Hashimoto, K., Asami, K., Kawashima, A., Habazaki, H., and Akiyama, E., The Role of Corrosion-resistant Alloying Elements in Passivity, *Corrosion Science*, Vol. 49, No. 1, p. 42-52, 2007.
- Hermawan, H., Dube, D., and Mantovani, D., Developments in Metallic Biodegradable Stents, *Acta Biomaterialia*, Vol. 6, No. 5, p. 1693-1697, 2010.
- Hofmann, J. and Sommer, K., Hygienic Design Von Anlagen und Deren Qualifizierungs Methoden, *Chemie Ingenieur Technik*, Vol. 78, No. 11, p. 1605-1614, 2006.
- Ladwein, T. and Gumpel, P., The Influence of Functional Properties of Stainless Steels on Corrosion, Houston, NACE Corrosion, Paper 04223, 2004.
- Lee, S. J., Lai, J. J., The Effects of Electropolishing (EP) Process Parameters on Corrosion Resistance of 316L Stainless Steel, *Journal of Materials Processing Technology*, Vol. 140, p. 206-210, 2003.
- Linden, J. and Rosen, J., US Patent, No. US 55827476, 2000.
- Ningshen, S., Kamachi, U., and Ramya, S., Corrosion Behavior of AISI Type 304L Stainless Steel in Nitric Acid Media Containing Oxidizing species, *Corrosion Science*, Vol. 53, No. 1, p. 64-70, 2011.
- Okado, J., Okada, K., Ishiyama, A., Setsuhara, Y., and Takenaka, K., Corrosion Resistance of Plasma-oxidized Stainless Steel, *Surface and Coatings Technology*, Vol. 202, No. 22, p. 5595-5598, 2008.
- Sharan, D., The Problem of Corrosion in Orthopedic Implant Materials, India, *Orthopedic Update*, Vol. 9, No. 1, p. 27-31, 1999.
- Shih, C. C., Shih, C. M., Su, Y. Y., Su, L. H., Chang, M. S., and Lin, S. J., Effect of Surface Oxide Properties on Corrosion Resistance of 316L Stainless Steel for Biomedical Applications, *Corrosion Science*, Vol. 46, No. 2, p. 427-441, 2004.
- Wallinder, D., Pan, J., Leygraf, C., and Delblanc, A., Electrochemical Investigation of Pickled and Polished 304L Stainless Steel Tubes, *Corrosion Science*, Vol. 42, No. 8, p. 1457-1469, 2000.
- Wu, W., Liu, X., Han, H., Yang, D., and Lu, S., Electropolishing of NiTi for Improving Biocompatibility, *Material Science and Technology*, Vol. 24, No. 6, p. 926-930, 2008.
- Zhao, H., Humbeck, J. V., Soheir, J., and Scheerder, D. I., Electrochemical Polishing of 316L Stainless Steel Slotted Tube Coronary Stents, *Materials Science: Materials in Medicine*, Vol. 13, No. 10, p. 911-916, 2002.
- Ziemniak, S. E., Hanson, M., Sander, P. C., Electropolishing Effects on Corrosion Behavior of 304 Stainless Steel at High Temperature, Hydrogenated Water, *Corrosion Science*, Vol. 50, p. 2465-2477, 2008.