

CORROSION BEHAVIOUR AND BIOCOMPATIBILITY OF 316 STAINLESS STEEL AS BIOMATERIAL IN PHYSIOLOGICAL ENVIRONMENT

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ABSTRACT

Although stainless steel is a material widely used for biomedical applications, its surface properties for long term application are still a serious concern. 316L stainless steel (SS 316L) is a material commonly used in dentistry for orthodontic braces, wires and in some cases as dental crowns. The pH value of natural saliva from the oral cavity can undergo sudden modification due to food products which are rich in citric acid. The electrochemical corrosion behavior of 316L stainless steel was evaluated in two simulated body fluid solutions, Fusayama-Mayer artificial saliva with pH=5 and Fusayama-Mayer artificial saliva adjusted with citric acid to a pH=1.58 which simulates the environmental conditions of the oral cavity. The surface of SS316L was investigated by optical microscope before and after corrosion assays. The electrochemical corrosion behavior was studied by open circuit potential, potentiodynamic polarization and linear polarization. Optical microscopy was used to characterize the corrosion damage after the electrochemical assays.

KEYWORDS: biomaterials, stainless steel, corrosion, simulated body fluids

1. Introduction

Man-made materials and devices have been developed to replace diseased or damaged parts (which become non-functional) in the human body in order to prolong life, to improve and restore tissue function, and to improve quality of life [1], through production of contact lenses, dental implants, artificial skin, heart valves, breast implants, joint prostheses or bone plates. Significant developments have been taking place to provide suitable biomaterials from metals/alloys, ceramics, bioglasses, and polymers with minimal reaction and rejection by the body [1].

It is well known that a series of interactions occur between the surface of biomaterials and the biological environment after they have been implanted into the human body. Therefore, the biomaterials surface plays an extremely important

role in the response of artificial medical devices to the biological environment [2]. The current research focuses on the biomaterials and the research community is aimed at understanding the fundamental processes at the interface between the implant surfaces and surrounding living tissues [2].

Table 1. shows the types, applications, and major failure mechanism of various biomaterials including metallic/alloys. However, each of these has some limitations. A single material cannot offer all desired properties; therefore, they have been used in combination with each other in the form of coatings and joints [1].

Metallic materials such as Ti, Ti-alloy, Co–Cr alloy and stainless steel–AISI (American Iron and Steel Institute) 316L are used as biomaterials due to their superior tensile and fatigue strength and fracture toughness as compared to nonmetals such as polymeric and ceramic. However, metallic materials

corrode by aggressive biofluid and release metallic ions which resulted in the reduction of their biocompatibility [1, 3]. The biocompatibility and corrosion resistance of these implants are primarily

determined by their constituent material and surface micro structural properties such as roughness, grain size, etc. [3].

Table 1. Types of biomedical materials and their applications [1]

Biomaterials	Objectives	Degradation mechanism	Applications
Metals/alloys: SS316L, Co-Cr alloy, Ti and Ti alloys, Ni-Ti alloys	Load bearing	Corrosion and mechanical	Fracture fixation plates, screws, pins, nails, joint replacements, orthodontic wires, femoral stems, cases for pacemakers, supports for heart valves, dental implants, dental crowns, bridges, fillings, and inner ear bone replacements
Ceramics: Carbon coatings, alumina, oxides, zirconia, glass, glass ceramics, and hydroxy apatite (HAP)	High hardness, wear resistance, and better bone bonding	Corrosion and mechanical	Carbon in heart valves, dental implants, joint implants, coatings for dental and joint implants, fill bone voids/cavities by HAP, tissue scaffolds, drug delivery systems, and inner ear implants
Polymer: Ultra high molecular weight polyethylene, polyester, polytetrafluoroethylene, PMMA, hydrogels, silicone rubber, PGA/PLA, collagen, cellulose, and chitosan	Articulating surfaces	Wear, swelling, leaching, chemical	Joint replacement, vascular grafts, bone cement, orthodontic devices (e.g. plates, dentures) contact and intraocular lenses, catheters, hand and toe joints, artificial tendon and ligament, reconstructive surgery, sutures, staples, tissue scaffolds, drug delivery systems, and hemostatic bandages, pace maker leads.

The stability of the surface oxide layer is one of the most important requirements of a biomaterial. For untreated 316L SS, the stability of the surface oxide layer is not very high and the possibility of metal ions being released is greater in comparison to Co-Cr and Ti-6Al-4V alloys [4]. After electrolytic polishing, 316L stainless steel forms a very thin, of a few-nanometer, compact oxide film resistant against corrosion in the presence of physiological human body fluids environments [5].

Among the metallic materials, AISI 316L stainless steel is most commonly employed for temporary devices such as fracture plates, bone screws and hip nails due to its low cost and acceptable biocompatibility [3, 6, 7]. It also has good ductility and possesses good biocompatibility [7, 8].

However, it has been often reported to suffer from severe crevice and galvanic corrosion, primarily due to the presence of occluded sites and high chloride concentration in physiological fluids.

The corrosion of the stainless steel implant releases metal ions such as Fe, Ni and Cr, which produce local systematic effects and thereby plays a role in prosthetic loosening [3].

In the dental industry, the metallic alloys are mainly used for crown, bridges, prostheses, supra- constructions and implants. They need to fulfill important requirements such as ease and reliability of

handling and treatment, toughness appropriate to the situation of application, good biocompatibility and aesthetic properties. These materials are confronted with extreme environmental conditions in the mouth, as the temperature can vary between 5 and 55 °C and the composition and the pH of the saliva varies depending on the nutrition [9]. The interactions between saliva and these foreign materials can affect the corrosion and tribocorrosion performance of 316L stainless steel prostheses [10].

The original artificial saliva solution was introduced by Takao Fusayama [10], but the chemical composition of artificial saliva has changed in time. Although saliva has a neutral acidity (pH of 7), due to the acidity of the modern western diet rich in citric acid from fruits and vegetables, saliva frequently becomes acidic (pH 5-6) during mastication. It is not uncommon for proteins, antibacterial agents and enzymes to be added to artificial organic solutions.

In recent years, there has been a significant increase in the number of studies examining the corrosion properties of 316L stainless steel used in medical/dental applications. In some recent studies the corrosion mechanisms of 316L stainless steel in various solutions, including different artificial saliva [10-13], have been examined. The aim of this study is to identify the occurring corrosion mechanisms where 316L stainless steel is exposed to an environment

with different pH values, which is similar to the oral cavity through electrochemical methods.

2. Experimental procedure

2.1. Materials

In this work it was analyzed 316L stainless steel with the chemical composition given in Table 2. Before corrosion examinations, the 316L stainless steel samples were polished with SiC #600 and diamond paste. The polish plates were degreased with alcohol and acetone and rinsed with distilled water. Afterwards the polished samples were dried with a hair dryer and inserted in corrosion holder to obtain a measurable surface of 1.76 cm².

2.2. Electrochemical behavior tests in bio-simulated fluid solution

In situ electrochemical measurements such as open circuit potential (OCP), linear polarization (Rp) and potentiodynamic polarization (PD) were carried out to access the anti-corrosive characteristics of 316L stainless steel in Fusayama-Mayer artificial saliva with two different pH. All electrochemical assays were performed using VoltaLab PGZ100 potentiostat/galvanostat and the data were recorded with VoltaMaster software.

The surfaces of SS 316L were investigated with an optical microscope type OPTIKA XDS-3MET before and after corrosion tests in order to confirm the results of electrochemical assays. The optical images were performed with software Vision Pro Plus, version 5.0 on computer connected to optical microscope.

Table 2. Chemical composition of 316L stainless steel

Element	Composition (wt.%)
C	0.02
Si	0.47
P	<0.007
S	<0.03
Cr	17.5
Mn	1.92
Cu	0.3
Ni	13.3
Mo	2.04
Nb	0.07
Fe	Balance

The electrochemical measurements were carried out in a conventional three electrodes cell shown in Fig. 1. consisting of Platinum-Rhodium grid as counter electrode (CE), Ag/AgCl (saturated solution of KCl, E=200 mV vs. Standard Hydrogen Electrode (SHE)) as reference electrode and 316L stainless steel as working electrode (WE).

The corrosion behavior of 316L stainless steel was tested in the Fusayama Mayer artificial saliva with pH=5 and respectively pH=1.58 adjusted with citric acid. Chemical compositions of these solutions are close to the natural saliva and contain different types of salts which are shown in Table 3.

The pH of Fusayama-Mayer artificial saliva was adjusted to 1.58 in order to understand the corrosion behavior of SS 316L under the worst-case conditions, although it is known that this pH value is much more aggressive than it would be normal for natural saliva.

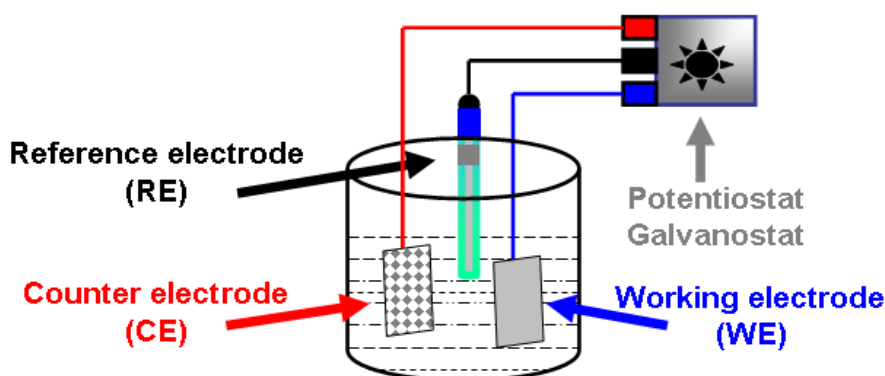


Fig. 1. Electrochemical cell set-up for corrosion tests

Table 3. Chemical composition of Fusayama-Mayer artificial saliva

Compound	Fusayama-Mayer artificial saliva
NaCl	0.4 g/L ⁻¹
KCl	0.4 g/L ⁻¹
CaCl ₂	0.8 g/L ⁻¹
Na ₂ HPO ₄	0.69 g/L ⁻¹
CH ₄ N ₂ O	1 g/L ⁻¹
Deionized water	Balance
pH	5

3. Results and discussion

3.1. Open Circuit Potential

The open circuit potential was monitored with the exposure time of 60 minutes, in order to obtain a stable potential vs. Ag/AgCl (reference electrode). The potential-time measurements are one of the ways to study the corrosion behavior of 316L stainless steel in the Fusayama-Mayer artificial saliva with two different pH values and recorded data are presented in Fig. 2.

From Fig. 2, it can be observed that the potential of 316L stainless steel immersed in the Fusayama-Mayer artificial saliva with two different pH values shift to positive values at the end of 60 minutes. The same Fig. 2. shows that the potential of sample immersed in the Fusayama-Mayer artificial saliva with pH=5, drops down slowly in the first 2 minutes due to the slow degradation of native passive layer from the surface and after that, it increases up to -90 mV at the end of studied time period. The potential of samples immersed in the modified Fusayama-Mayer artificial saliva with pH=1.58, the potential decreases faster in the first 5 minutes due to the rapid

degradation of passive film and after that increases slowly up to value of -120 mV.

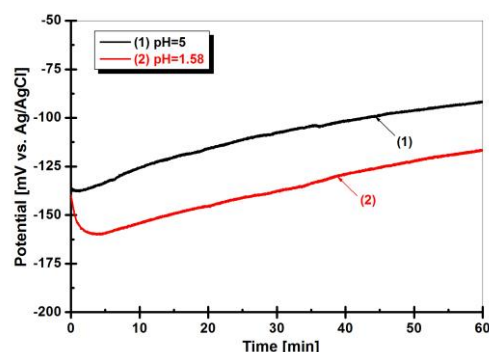


Fig. 2. Open circuit potential plots obtained in: (1) Fusayama-Mayer artificial saliva pH=5.0 and (2) Fusayama-Mayer artificial saliva adjusted with citric acid at pH=1.58

This increasing trend of potential has been observed by T. Hryniewicz [14] for 316L stainless steel after immersion in a Ringer solution. The increasing trend of 316L stainless steel potential reveals the formation of a stable passive oxide layer on the sample surface.

3.2. Evolution of polarization resistance (R_p) values during immersion time

The linear polarization method was used to evaluate the polarization resistance of 316L stainless steel in the Fusayama-Mayer artificial saliva with two different pH values. The evaluation of polarization resistance was measured around open circuit potential value with a very small potential amplitude (± 40 mV) in order to preserve the steady state surface.

Fig. 3 (a) presents the polarization resistance diagrams of SS 316L immersed in Fusayama-Mayer artificial saliva with pH=5 and 1.58, respectively.

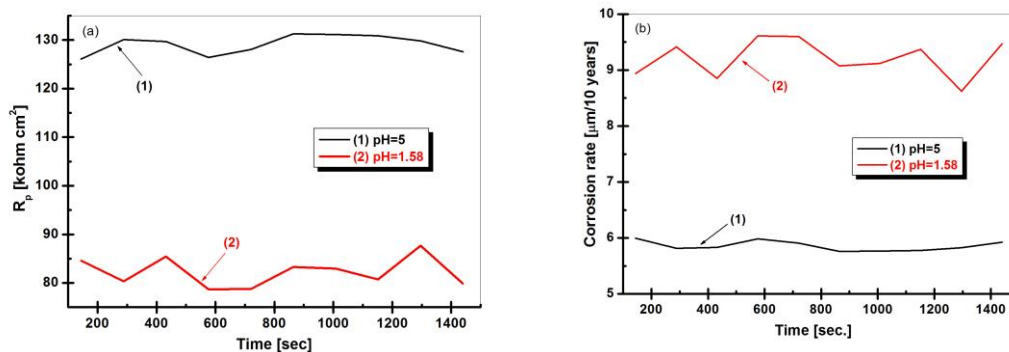


Fig. 3. (a) The evolution of polarization resistance (R_p) and (b) the evolution of corrosion rate values during the immersion in Fusayama-Mayer artificial saliva with (1) pH=5 and (2) pH=1.58

Fig. 3 (a). shows that the polarization resistance value of SS 316L, immersed in Fusayama-Mayer with pH=5, is equal to $130 \text{ kohm}\cdot\text{cm}^2$. In comparison, the polarization resistance value of SS 316L immersed in the Fusayama-Mayer artificial saliva adjusted with citric acid to a pH value of 1.58 is equal to $80 \text{ kohm}\cdot\text{cm}^2$. The increased polarization resistance value means that the formed passive film after immersion in the Fusayama-Mayer artificial saliva with pH=5 is more resistant compared with that formed in low pH value equal to 1.58. A decrease of the polarization resistance value at once with the decrease of pH value lead to the increasing of the corrosion current density and therefore to a higher corrosion rate, as noticeable in Fig. 3 (b). Fig. 3 (b) presents the corrosion rates versus the time corresponding to SS 316L surfaces immersed in the Fusayama-Mayer artificial saliva with two different pH values. According with the data plotted in Fig. 3 (b). the higher corrosion rate is shown to correspond to SS 316L immersed in the Fusayama-Mayer artificial saliva with the lowest pH value (pH=1.58) in comparison with the corrosion rate of SS 316L immersed in the Fusayama-Mayer artificial saliva with pH=5. These results show that the SS 316L has a lower corrosion resistance in the Fusayama-Mayer artificial saliva (pH=5) and are in good agreement with the evolution of open circuit potential values.

3.3. Potentiodynamic polarization

The potentiodynamic polarization studies were recorded in a range of potential starting from -1.5 V vs. Ag/AgCl to +1.5 V vs. Ag/AgCl at a scan rate of 5 mV/s. Fig. 4. shows the potentiodynamic polarization of SS 316L after immersion in the Fusayama-Mayer artificial saliva with two different pH value, 5 respectively 1.58.

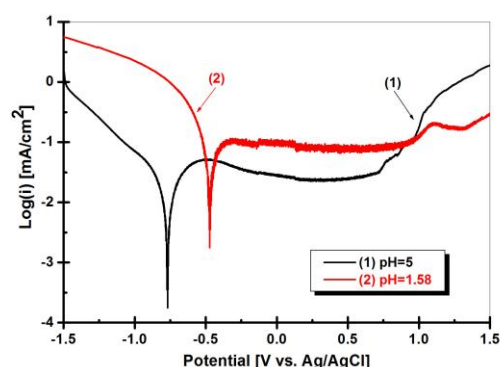


Fig. 4. Tafel representation of potentiodynamic polarization for SS 316L immersed in Fusayama-Mayer with (1) pH=5 and (2) pH=1.58

Table 4. The electrochemical corrosion data extracted from the electrochemical corrosion polarization curves

Sample/ Solution	$E_{corr} (i=0)$ (mV vs. Ag/AgCl)	R_p kohm. cm^2	i_{corr} mA. cm^2	b_a (mV vs. Ag/AgCl)	b_c (mV vs. Ag/AgCl)
SS 316L/ Fusayama-Mayer pH=5	-770	3.25	11.21	241.4	-214.4
SS 316L/ Fusayama-Mayer with citric acid pH=1.58	-472.7	1.16	52.49	380.2	-146.8

The anodic Tafel constant β_a and cathodic Tafel constant β_c , as well as the corrosion current density I_{corr} , were calculated from the intersection of the anodic and cathodic Tafel lines in the polarization curves at E_{corr} [15, 16].

The results are listed in Table 4. Fig. 4. shows that the corrosion current (i_{corr}) of SS 316L immersed in the Fusayama-Mayer artificial saliva with pH value equal to 1.58 is higher than the corrosion current of SS 316L immersed in Fusayama-Mayer artificial saliva with pH value equal to 5 which provoked the

decreasing of the corrosion rate from $3.25 \text{ kohm}\cdot\text{cm}^2$ to $1.16 \text{ kohm}\cdot\text{cm}^2$ with decreasing of pH value.

3.4. Optical microscopy

The surfaces of SS 316L were investigated before and after corrosion tests in the Fusayama-Mayer artificial saliva with the pH value equal to 5 and Fusayama-Mayer artificial saliva adjusted with citric acid and the pH value equal to 1.58 in order to estimate the corrosive effects and are presented in Fig. 5.

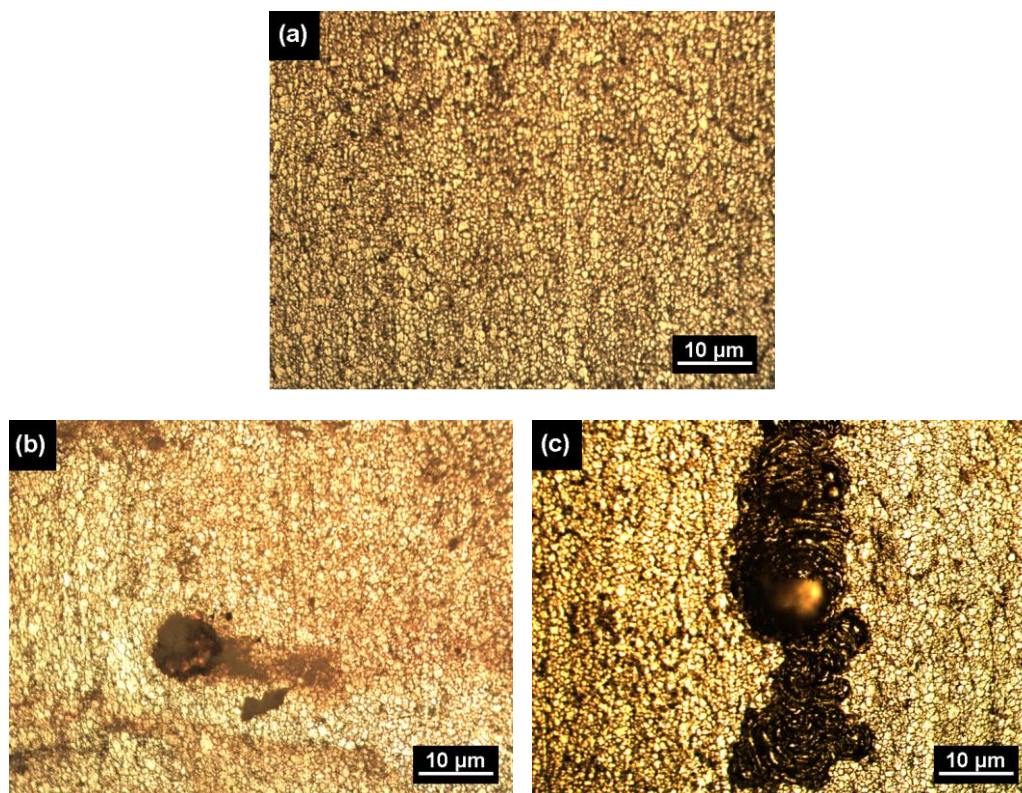


Fig. 5. Optical microscopy of SS 316L (a) before corrosion, (b) after corrosion in Fusayama-Mayer artificial saliva with pH=5 and (c) after corrosion in modified Fusayama-Mayer artificial saliva with citric acid and pH=1.58

Fig. 5 (a). shows that before corrosion tests the SS 316L has a uniform surface with no defects. After corrosion tests in Fusayama-Mayer artificial saliva with pH=5 (Fig. 5 (b)), the 316L stainless steel undergo small diameters pits and a few rust spots are visible in comparison with the 316L stainless steel surface (Fig. 5 (a)) before corrosion assays.

The samples of 316L stainless steel surface immersed in Fusayama-Mayer artificial saliva adjusted with citric acid and whose pH value is equal with 1.58, present severe pitting damage (Fig. 5 (c)) in comparison with the samples immersed in Fusayama-Mayer artificial saliva with the pH value equal with 5. The pitting damage covers a high surface of the 316L stainless steel samples and the pits are deeper into the substrate.

4. Conclusion

The corrosion behavior of Stainless Steel 316L was investigated in simulated body fluid – Fusayama-Mayer Artificial Saliva at different pH values.

The experimental results reveal that the SS316L present a better corrosion behavior in the Fusayama-Mayer Saliva with pH=5 in comparison with the

Fusayama-Mayer Saliva modified with Citric Acid and pH=1.58.

From the linear polarization curves it can be seen that the decreasing of pH from 5 to 1.58 produce a decrease of polarization resistance (R_p) from $130 \text{ kohm}\cdot\text{cm}^2$ to $80 \text{ kohm}\cdot\text{cm}^2$.

The optical microscopy images are in good agreement with electrochemical measurements.

Acknowledgements

UEFISCDI - Ministry of Education and Research is acknowledged for the financial support to Competences Centre Interfaces - Tribocorrosion and Electrochemical Systems (CC-ITES) - Dunarea de Jos University of Galati - Research Project: *HyBioElect*, contract 10 /30-08-2013 (2013 - 2016) in the frame of National Research Programme Romania - PN II PCE.

References

- [1]. R. Singh, N. B. Dahotre, *Corrosion degradation and prevention by surface modification of biometallic materials*, Journal of Materials Science: Materials in Medicine, 18, p. 725-751, 2007.

- [2]. X. Liu, P. K. Chu, C. Ding, *Surface nano-functionalization of biomaterials*, Materials Science and Engineering R 70, p. 275-302, 2010.
- [3]. S. K. Tiwari, T. Mishra, M. K. Gunjan, A. S. Bhattacharyya, T. B. Singh, R. Sing, *Development and characterization of sol-gel silica-alumina composite coatings on AISI 316L for implant applications*, Surface & Coatings Technology, 201, p. 7582-7588, 2007.
- [4]. T. P. Singh, H. Singh, H. Singh, *Characterization, corrosion resistance, and cell response of high-velocity flame-sprayed HA and HA/TiO₂ coatings on 316L SS*, Journal of Thermal Spray Technology, 21, p. 917-927, 2012.
- [5]. T. Hryniewicz, R. Rokicki, K. Rokosz, *Surface characterization of AISI 316L biomaterials obtained by electropolishing in a magnetic field*, Surface & Coatings Technology, 202, p. 1668-1673, 2008.
- [6]. A. Mahapatro, *Bio-functional nano-coatings on metallic biomaterials*, Materials Science and Engineering C 55, p. 227-251, 2015.
- [7]. A. Parsapour, S. N. Khorasani, M. H. Fathi, *Effect of surface treatment and metallic coating on corrosion behavior and biocompatibility of surgical 316L stainless steel implant*, Journal of Materials Science Technology, 28, p. 125-131, 2012.
- [8]. J. Yang, F. Cui, I.S. Lee, X. Wang, *Plasma surface modification of magnesium alloy for biomedical application*, Surface & Coatings Technology, 205, p. S182-S187, 2010.
- [9]. W. D. Mueller, C. Schoepf, M. L. Nascimento, A. C. Carvalho, M. Moisel, A. Schenk, F. Scholz, K. P. Lange, *Electrochemical characterization of dental alloys: its possibilities and limitations*, Analytical and Bioanalytical Chemistry, 381, p. 1520-1525, 2005.
- [10]. A. Hayes, S. Sharifi, M. M. Stack, *Micro-abrasion-corrosion maps of 316L stainless steel in artificial saliva*, Journal of Bio- and Tribo-Corrosion, 1, p. 1-15, 2015.
- [11]. K. Hajizadeh, H. Maleki-Ghaleh, A. Arabi, Y. Behnamiam, E. Aghaie, A. Farrokhi, M. G. Hosseini, M. H. Fathi, *Corrosion and biological behavior of nanostructured 316L stainless steel processed by severe plastic deformation*, Surface and Interface Analysis, 47, p. 978-985, 2015.
- [12]. Y. Kayali, A. Buyuksagis, Y. Yalcin, *Corrosion and wear behaviors of boronized AISI 316L stainless steel*, Metals and Materials International, 19, p. 1053-1061, 2013.
- [13]. B. Al-Mangour, R. Mongrain, E. Irissou, S. Yue, *Improving the strength and corrosion resistance of 316L stainless steel for biomedical applications using cold spray*, Surface & Coatings Technology, 216, p. 297-307, 2013.
- [14]. T. Hryniewicz, R. Rokicki, K. Rokosz, *Electrochemical and XPS studies of AISI 316L stainless steel after electropolishing in a magnetic field*, Corrosion Science, 50, p. 2676-2681, 2008.
- [15]. L. Benea, E. Mardare-Danaila, M. Mardare, J. P. Celis, *Preparation of titanium oxide and hydroxyapatite on Ti-6Al-4V alloy surface and electrochemical behavior in bio-simulated fluid solution*, Corrosion Science, 80, p. 331-338, 2014.
- [16]. K. F. Khaled, S. S. Abdel-Rehim, *Electrochemical investigation of corrosion and corrosion inhibition of iron in hydrochloric acid solutions*, Arabian Journal of Chemistry, 4, p. 397-402, 2011.