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ICP- MS DETERMINATIONS IN SUSTAINING CORROSION DATA OF 316 STAINLESS STEELS IN BIOLIQUIDS

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The paper is focused on ICP-MS (inductively coupled plasma – mass spectroscopy) and electrochemical determinations of 316 stainless steels behavior in bioliquids, in order to evaluate their stability in PBS (phosphate buffered saline) and HFS (human female serum). The investigated stainless steels were 316 and 316L. Electrochemical procedures were Tafel plots and electrochemical impedance spectroscopy (EIS). Based on electrochemical and ICP-MS data it was established that the overall corrosion resistance property of the 316L stainless steel is better than that of the 316 in either PBS or HFS solution.

Keywords: ICP-MS, EIS technique, stainless steel 316, corrosion, Tafel polarization curves, stainless steel

1. Introduction

Despite the fact that CoCr alloys [1] and titanium alloys [2, 3] are widely used nowadays, having better properties and better behavior as implant materials, the uncoated [4] and coated stainless steel materials [5-7] are still investigated for the use in oral cavity and orthopedic applications, being much cheaper. The behavior of 316L stainless steel in simulating physiological conditions has been studied by various authors [8, 9].

The dissolution/corrosion properties of the steels can also be enhanced by various surface coatings [5-7] to strengthen the protective properties of the passivation layer. The data on the release of metal ions provides information on the potential bioaccessibility of components. Bioaccessibility means the potential for a substance to come in contact with a living organism and interact with it (IUPAC glossary of terms used in toxicology).

Taking into account that even in a small amount the metal ions release in the body could be very aggressive due to their migration and accumulation in different organs, sometimes far away from the point of release, it is very

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important to quantify the amount of ion release in various environments, and the present paper is aiming in such investigation using ICP-MS determinations [10]. Due to the fact that quantification in time of the amount of ion release in a specific media is related to corrosion rate in such media, the present research is a procedure to sustain electrochemical procedures in evaluation of 316L stability in bioliquids.

2. Test materials and methods for investigation

2.1. Materials

The chemical composition of the stainless steel used in this study is given in Table 1. Stainless steels were provided from Beznoska Co. Czech Republic.

Table 1

Chemical composition of stainless steels, wt%

Sample	C	Si	Mn	Cr	Fe	Mo	N	P	Co	Ni
SS316	0.039	0.22	4.07	16.85	60.57	2.30	0.08	0.024		10.92
SS316L	0.023	0.36	1.9	17.05	62.86	2.82	0.09	0.018	-	14.87

The sample surfaces were wet gradually polished using 120, 220, 320, 600, 800, 1000, and 1200 grit silicon carbide papers to get flat and scratch-free surface. These samples were then rinsed with water, and ultrasonically cleaned for 30 minutes using ethanol as a medium.

2.2. Solutions

The chemical composition of the phosphate buffer saline (PBS) solution is (in g/L) 8 NaCl, 0.2 KCl, 1.15 Na_2HPO_4, and 0.2 KH_2PO_4 according to ASTM standards F2129 [11].

The human female serum (HFS) components are in the following concentrations: total bilirubin 0.45mg/dL, direct bilirubin 0.1 mg/dL, cholesterol 245 mg/dL, glucose78 mg/dL, creatinine 1.17 mg/dL, uric acid 4.94 mg/dL, urea 44.5 mg/dL, trigicerides 144 mg/dL, GPT (glutamic-pyruvic transaminase) 49 U/L, GOT (glutamic oxaloacetic transaminase) 51 U/L, LDH (lactate dehydrogenase) 593 U/L, GGT (gamma-glutamyl transpeptidase) 26 U/L, magnesium 2 mg/dL, calcium 8.3 mg/dL, iron 125 mg/dL.

2.3. Methods

Various methods have been used to evaluate the corrosion resistance of various artificial medium.

The electrochemical measurements were carried out in 100 mL electrolytes at 37°C using a potentiostat/galvanostat VoltaLab 40 controlled by a computer. The potentials were refered against a saturated calomel electrode and a platinum electrode was used as an auxiliary electrode. The electrochemical measurements were carried out immediately after the sample polishing and cleaning. Tafel plots for various specimens were obtained by exposing them into bioliquids and polarizing from -1V to +1V vs. SCE with scan rate of 2 mV/s.

EIS (electrochemical impedance spectra) data were obtained with *ac* signal amplitude of 10 mV in the frequency range of 10^{-2} to 10^{4} Hz.

In order to determine the biodegradation of alloys, the concentration of dissolved metal ions (Fe, Cr, Ni, Mo, Ti, Al and V ions) in physiological media was measured using inductively coupled plasma – mass spectroscopy (ICP-MS).

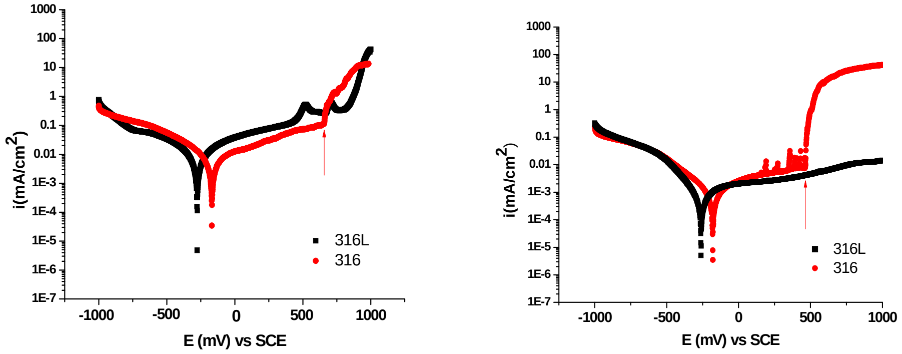
Stainless steel 316L and 316 plates were immersed in 100 mL of body fluid and simulated body solution contained in sterile plastic tubes. The immersion test lasted for 45 days. During the immersion period, 1 mL of solution aliquot was taken from each solution after the following immersion periods: 3, 5, 7, 9, 15, 25, 35 and 45 days. All the ICP-MS measurements were carried out in triplicate at room temperature.

3. Results and discussion

3.1. Tafel plots

Corrosion current density is commonly utilized as an important parameter to evaluate the kinetics of corrosion reactions.

In Fig.1 the potentiodynamic polarization curves are presented, showing the corrosion behavior of 316L and 316 stainless steel in PBS and HFS solutions.



a) b)

Fig 1. Polarization curves for 316 and 316L in a) PBS and b) HFS

These polarization curves can be divided in several potential domains: the cathodic domain where the current can be assigned to the reduction of water and partially of dissolved oxygen reduction, the potential domain characterized by the transition from cathodic to anodic current at the corrosion potential and the third domain corresponds to the passive plateau, followed by a region where passivity was broken due to pitting corrosion.

It can be easily seen the best performance in corrosion behavior of 316L stainless steel in both solutions. The range of passivation appears to be shorter for 316 than for 316L. The arrow indicates the beginning of pitting, which occurs for 316 at less positive potentials than for 316L.

The corrosion current density (i_{corr}), corrosion potential (E_{corr}), Tafel slopes (β_a, β_c), polarization resistance (Rp) and rate of corrosion (v_{corr}) obtained from the Tafel curves are shown in Table 2 and Table 3.

Table 2

Corrosion parameters for 316L and 316 stainless steel in phosphate buffered saline (PBS)

Sample	E_{cor} (V)	β_a (mV/dec)	β_c (mV/dec)	i_{corr} ($\mu A/cm^2$)	v_{corr} ($\mu m/y$)	R_p($k\Omega \times cm^2$)
316L	-279	159.7	-155	3.6107	41.9	7.09
316	-174	178.2	-142	5.198	60.3	4.77

Table 3

Corrosion parameters for 316L and 316 stainless steel in human female serum (HFS)

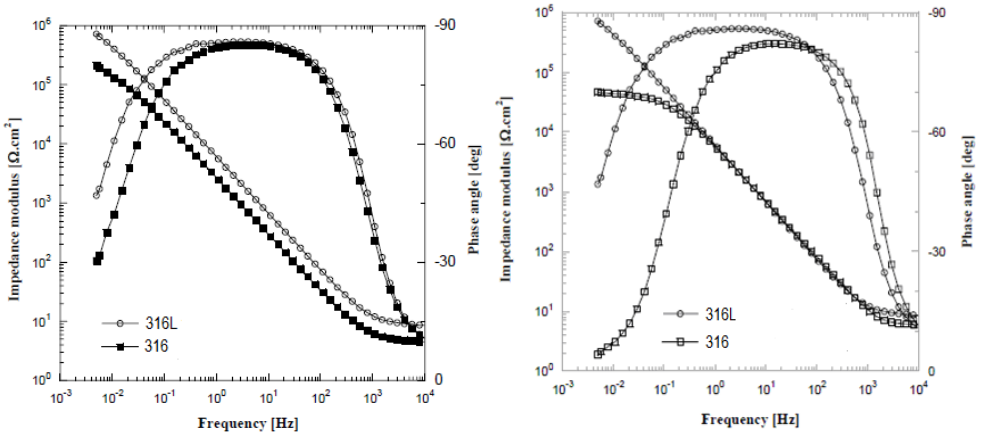
	E_{cor} (V)	β_a (mV/dec)	β_c (mV/dec)	i_{corr} ($\mu A/cm^2$)	v_{corr} ($\mu m/y$)	R_p($k\Omega \times cm^2$)
316L	-171	171	-151	1. 79	20.77	13.84
316	-260	116	-75	2.96	34.4	23.06

The results of the tests indicate that lower corrosion rate for both stainless steel samples is in the HFS solution comparative with PBS solution

3.2. Electrochemical impedance spectroscopy (EIS) measurements

The EIS plots measured at open circuit potentials are given in Bode format in Fig. 3.

The 316L alloys exhibit high impedance values of the order of 10^6 Ωcm^2, indicating high corrosion resistances in the both solutions. The 316L exhibits negative phase angles close to 80-90^0 at medium and low frequencies, suggesting the formation of compact passive film at the interface. However, the phase angles of the 316 steel in PBS solution are dropped to about -50^0 at lower frequencies. Such a behavior indicates that the passive film formed on the 316 alloy is defective in PBS solution.



a) b)

Fig 2. Bode plots for 316 and 316L in a) HFS and b) PBS

3.3. Determination of metal ion release from 316 and 316 L stainless steels

The evolution in time of concentrations of metal ions (Fe, Cr, Ni and Mo) released by corrosion from stainless steel 316L in natural body fluid (HFS) and in phosphate buffered saline solution (PBS) are presented in Figs. 3 and 4.

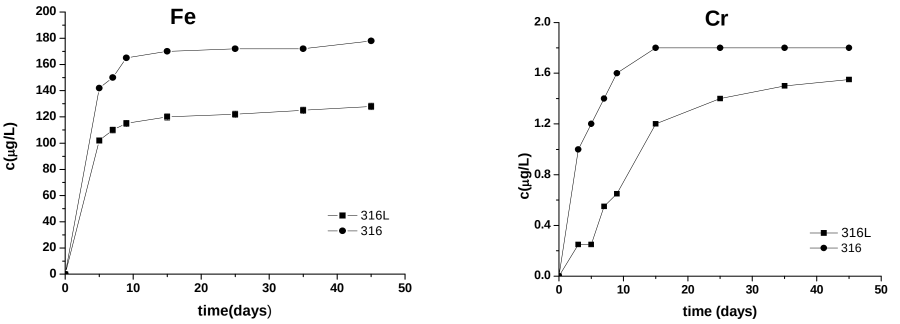


Fig. 3. The evolution in time of ion release from 316L and 316 stainless steel in HFS - Fe and Cr

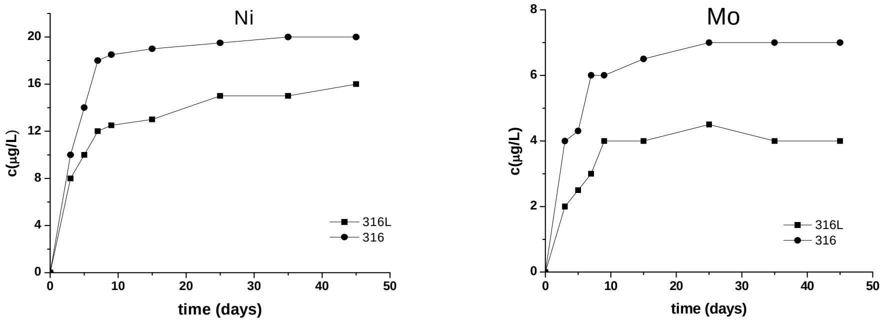


Fig. 3. The evolution in time of ion release from 316L and 316 stainless steel in HFS - Ni and Mo

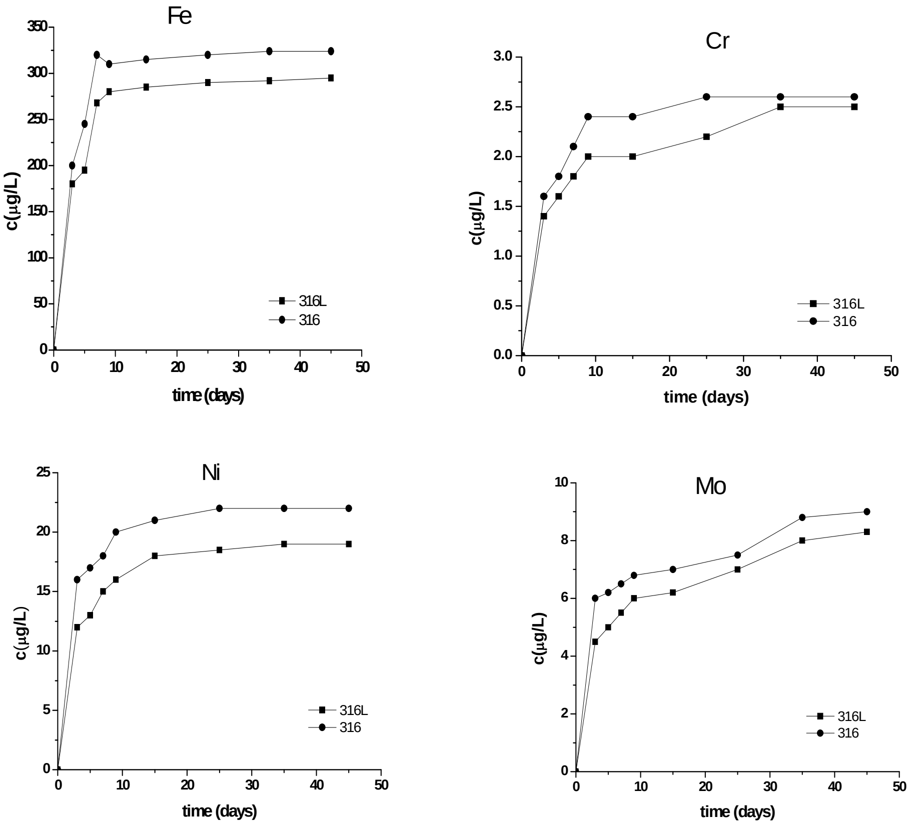


Fig. 4. The evolution in time of ion release from 316L and 316 stainless steel in PBS

The ions release versus time for all measurements has a step with initial rise followed by a slow increase, and then it nearly becomes constant, suggesting a steady state established during the dissolution process [13].

Iron is released in the highest concentration, approximately 10-fold higher than the concentration of nickel, the next most dissolved metal. The total release rate was highest in the beginning of exposure (during the first 10 hours) and decreased with time for longer incubation. This can be explained by the increase in the chromium content in the layer of alloy remained on the surface of the metal which favors the formation of insoluble products. The concentrations of released metal ions decrease in the following order: Fe > Ni > Mo > Cr.

The passive layer formed on the surface of the alloy 316L contains products with large concentrations of chromium and iron species and small amounts of nickel and molybdenum species, as oxides and hydroxides [14, 15]. The ratios of ionic species in solutions should be compared with ratios of alloying elements calculated from the chemical composition of stainless steel 316L and 316.

When calculating the ratios of dissolved metal ions measured by ICP-MS after 45 days (Table 4), it can be conclude that iron is dissolved preferentially and chromium is dissolved in concentrations lower than would be expected considering its concentration in the alloy, as evidenced by the lower measured values.

Table 4

The ratios of alloying elements as metal ions released in bioliquids after 45 days of immersion. The ratios of corresponding percentage ratios in the sample alloy are in parenthesis

	316L		316	
	HFS	PBS	HFS	PBS
$\frac{\text{Fe}}{\text{Cr}}$	82.58 (3.68)	118 (3.68)	95.55 (2.81)	124.61 (2.81)
$\frac{\text{Fe}}{\text{Ni}}$	8 (4.22)	15.52 (4.22)	9.05 (5.54)	16.72 (5.54)
$\frac{\text{Fe}}{\text{Mo}}$	32 (22.29)	35.97 (22.29)	34.57 (26.33)	36 (26.33)
$\frac{\text{Cr}}{\text{Ni}}$	0.09 (1.14)	0.13 (11.14)	0.09 (1.97)	0.15 (1.97)
$\frac{\text{Cr}}{\text{Mo}}$	0.38 (6.04)	0.30 (6.04)	0.25 (9.33)	0.32 (9.33)

Whereas in the 316L stainless steel the ratio Fe/Cr is 3.68 after 45 days of immersion in HFS solution it reaches values of 82.58 and in PBS the value was 118 showing the preferential dissolution of iron in PBS solution. The same trend was observed for 316 stainless steel. In the case of Fe/Ni ratios, the highest values are obtained for 316 stainless steel in PBS.

The total rates of weekly metal release from 316L in PBS and HFS are approximately 330 μg/L and respectively 130 μg/L and in the case of 316 stainless steel they are 346 μg/L in PBS and 190 μg/L in HFS. These results are in compliance with experimental data obtained by other authors [16].

The quantity of total metal released depends on pitting resistance equivalent (PRE), PRE = % Cr + 3.3% Mo + 16% N [17]. The PRE values of 316L, and 316 stainless steels are approximately 25% and 27%, respectively. Therefore, the weekly quantity of total metal released from 316L is the lowest metal release by considering the corrosion of both stainless steels.

The only ion taken up by red blood cells following corrosion is Cr^{6+}. Ni ionic species is very small in dimensions and has a low affinity for blood cells. Despite the fact that Ni is an essential element in body, the maximum daily intake should not exceed ~500 μg, and threshold concentration of ~30 ppm being required to trigger any cytotoxic response. In this study, observed Ni levels are negligible compared with daily intake of Ni.

Comparing the experimental data we can conclude that PBS solution is a more aggressive medium than HFS. This observation is consistent with the data obtained from Tafel curves from which there is deduced that the two stainless steel present the higher corrosion rate in PBS than in HFS.

4. Conclusions

The overall corrosion resistance property of the 316L stainless steel is better than that of the 316 in HFS bioliquid or PBS solution. This conclusion is related to the concentrations of the ions released which are smaller in HFS than in PBS for the both studied stainless steels. Regarding the total rates of weekly metal release from 316L in PBS and HFS are approximately 330μg/L and respectively130 μg/L and in the case of 316 stainless steel they are 346 μg/L in PBS and 190 μg/L in HFS

Taking into account the evolution in time of ion release with a trend to steady state in all the cases, it demonstrates an oxide barrier formation which is a motivation for electrochemical stability as well; therefore, we can conclude that ICP-MS analysis technique is sustaining the electrochemical data.

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