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Novel composite material using porous sintered stainless steel for orthodontic applications

MARIA MARCU[1], ALEXANDRA BANU[2], MIRCEA CORBAN[3]
[1]Institute f Physical Chemistry "Ilie Murgulescu", Splaiul Independentei 202, Bucharest ,

[2] Politehnica University of Bucharest, Splaiul Independentei 313, Bucharest, Romania
[3]Metav C&D, C.A. Rosetti 31, Bucharest, Romania

Abstract

This paper presents a comparative study of the electrochemical behavior of AISI 316L stainless steel samples, rolled (PM) and powder metallurgy (PM) processed in Fusyama artificial saliva.

Open-circuit potential, polarization curves and impedance spectroscopy are the electrochemical procedures selected for this work. The samples microstructural and microcompositional characteristics were analyzed by scanning electron microscopy (SEM).

Electrochemical investigations revealed the specific influence of the sintering material microstructure and porosity on its electrochemical characteristics.

The 316L stainless steel is known as susceptible to localized corrosion by pitting or crevice; this susceptibility is emphasized by the presence of the mechanical tensions.

The results of the localized corrosion chemical test suggest the necessity of improvement of the sintering by the length extension of this operation.

These aspects argue the possibility of an advantageous use of PM material in applications reserved until now only to the rolled material, especially from dentistry applications.

Keywords: biomaterials, stainless steel, corrosion, sintered material.

Introduction

Metals are used in many medical implants and prostheses because of their strength and durability. However, the success or failure of the implant is largely dependent on the design of the implant, surgical expertise, and corrosion resistance [1].

Nowadays, a number of different alloys are used in dentistry for fillings, fixed and mobile prosthetic works, orthodontic devices and dental implants. Applied alloys in a mouth are exposed to the influence of chemical, biological, mechanical, thermal and electrical forces. These forces have a negative effect on functional and esthetic characteristics of dental works and they substantially lessen their durability. Electrochemical corrosion [2] is the most important damaging factor of dental works. Corrosion is the unintentional wearing down of the metal surfaces, and damage to the outer and inner layers of their surface caused by exposure to chemical or electrochemical reaction of the surrounding area. Electrolyte is needed for electrochemical reaction. Saliva, as well as soft and a hard tissue, has the role of electrolyte in the mouth. Saliva is a media of strong corrosive affect. The corrosion potential of saliva increases as its pH factor decreases and as chloride concentration increases [3].

Some features define it as an ideal biomaterial for orthopedic and maxillofacial surgery including a biocompatible chemical composition avoiding adverse tissue reactions, acceptable strength, a high wear resistance to minimize wear debris, adequate corrosion resistance in the physiological milieu and an elasticity modulus similar to that of bone in minimizing bone resorption around the implant [4]. Austenitic stainless steel conforming to the ASTM specification F138 is currently used for orthopedic device manufacture and it is a variation of the traditional AISI 316L steel, characterized by a lower non-metallic content (3). Stainless steel has been demonstrated to have acceptable biocompatibility and physical properties, and can be manufactured in a variety of shapes and sizes for wires and screws.

In developing new materials for orthodontic applications it would be of great interest to use the new techniques to fabricate the materials where enhanced properties are required as compared to the stainless steel alloy.

Powder metallurgy is a suitable technology to fabricate complex parts with net shaping capabilities, appreciable dimensional precision and high productivity [5]. Sintered stainless steel is generally used in special applications, where enhanced properties are required as compared to the low alloy steel. However the wider application of sintered stainless steel is limited due to their poor mechanical and corrosion properties.

Biocorrosion has been considered a problem for the long durability of implants in human bodies and the release of metal ions can cause adverse physiological effects, toxicity, carcinogenicity and metal allergy. The aim of this study is to examine the behavior of both types of stainless steel used for dental alloys in artificial saliva under corrosion, and also to compare their specific electrochemical properties.

Materials and Methods

A commercially available, compacting grade of 316L stainless steel powders and a sample obtained from a laboratory casting materials was used in the study. 316 stainless steel powder was obtained by atomization with water. Some typical data of this powder are: apparent density: 2,80g/cm^3, flow 29sec./50g. The powder was pressed in a rigid die with the specific force of 6000daN/cm^2. The sample was then sintered at 1300^{o}C, in vacuum. The sample sinter density is 6,52 g/cm^3. On the route of sintering process, the complex phenomena appear, assuring joining the metal powder particulate by diffusion in the absence of the liquid phase in this case. The initial raw aspect of a “316S” sample micro zone is presented in figure 1.

Table 1 and 2 present the chemical composition for casting and sintered sample.

Table 1. Properties of the base alloy AISI 316 L, wt %

Element	Cr	Ni	Mo	Mn	Si	Cu	N_2	C	P	S	Fe
%	18	14	2	2	1	0,5	0,1	0,03	0,025	0,01	base

Tabel 2. Properties of the base alloy powder (316L), wt %

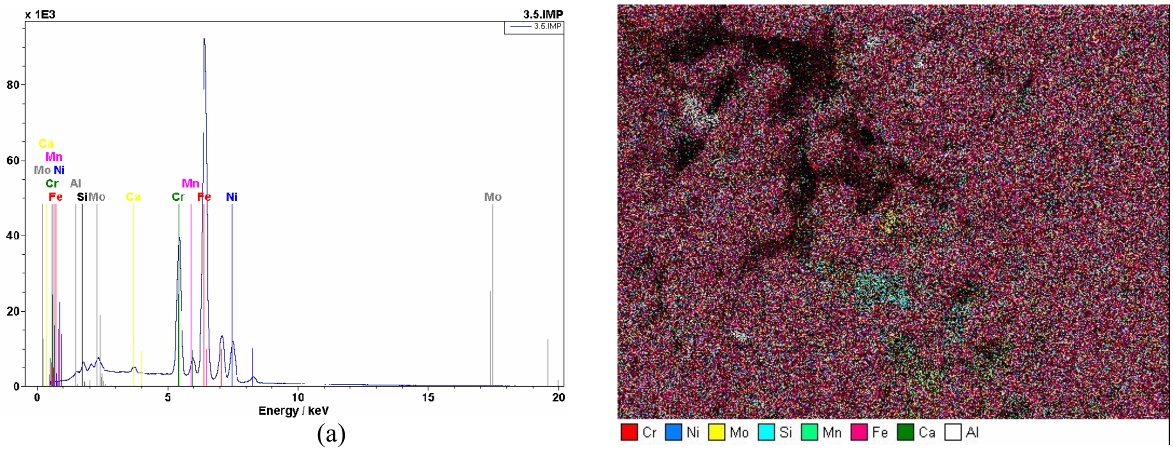
Element	C	Cr	Ni	Mo	Si	Fe
%	0,02	17	13	2,2	0,8	base

The sample's surface was prepared by mechanical polishing with emery paper and silica powder and finally rinsed with distilled water and ultrasonically cleaned in izoprolilic alcohol and finally dried in argon.

The study of the electrochemical behaviour of biomedical materials in artificial saliva type Fusayama&Meyer [6], was carried out using open circuit-potential, potentiodynamic polarization curves, potentiostatic measurements at different immersion times and electrochemical impedance spectroscopy (EIS).

The electrochemical experiments were carried out using a Gamry computerized equipment, in a conventional three electrode glass cell provided with a saturated Hg/Hg_2Cl_2//KCl, and a platinum electrode as reference and auxiliary electrodes respectively.

1. **Corrosion potential –time measurements** were performed during 250 hours of exposure according to static immersion method, in artificial saliva at pH=6 and 37.2°C. Simultaneously, weight loss of the samples was measured and at the end of the exposure time by AAS analytical methods.
2. **Potentiodynamic polarization** was performed in the potential range from -200mV to +1000mV, with a scan rate of $150 mVmin^{-1}$ for electrochemical and corrosion parameters measurements at different pH values;
3. **Electrochemical Impedance Spectroscopy** measurements were carried out in the frequency range from 100KHz to 0.01Hz at zero, at the different time of exposure in artificial saliva.
4. **Structural analysis** measurements represent a quantitative analysis for establish the composition of sintered alloy, the elements and the blisters distribution (**figure 1**).



(a)

(b)

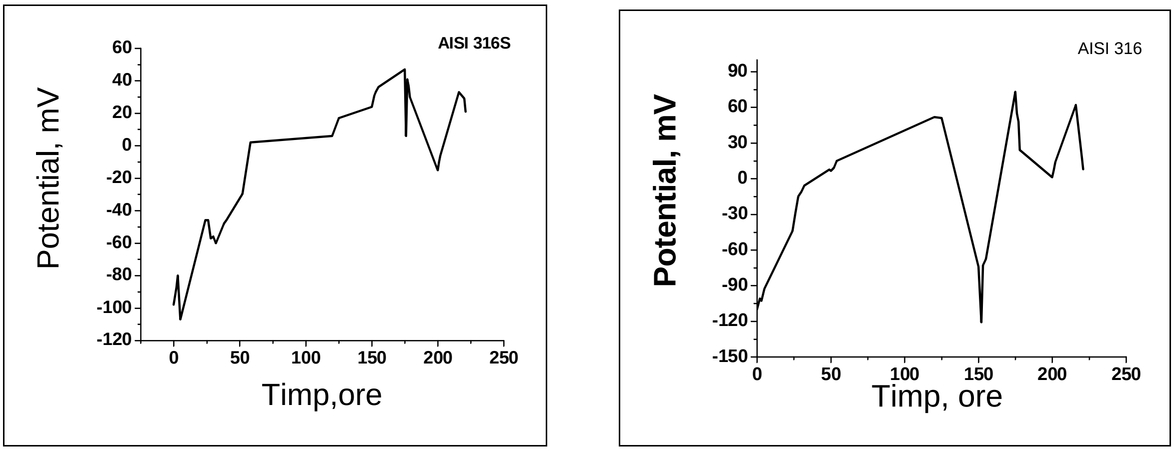
Figure 1. The composition of sintered alloy sample: (a), Quantitative chromium distribution (b), EDX spectrum.

The EDX chemical microanalysis of this area confirmed the general chemical composition of the material, (**Figure1**), and the uniform chromium repartition, the same aspect characterize also, nickel, manganese and silicon.

Results and Discussion

Corrosion investigations were performed to obtain:
(1) Open circuit potential OCP
(2) Electrochemical impedance spectroscopy EIS, and
(3) Potentiodynamic polarization curves.

The corrosion measurements data were obtained in the range of potentials from −400 mV to 1000 mV recorded with the rate of 150 mV/min. Subsequently, we investigated the polarization curves, and having them the corrosion rates were calculated.

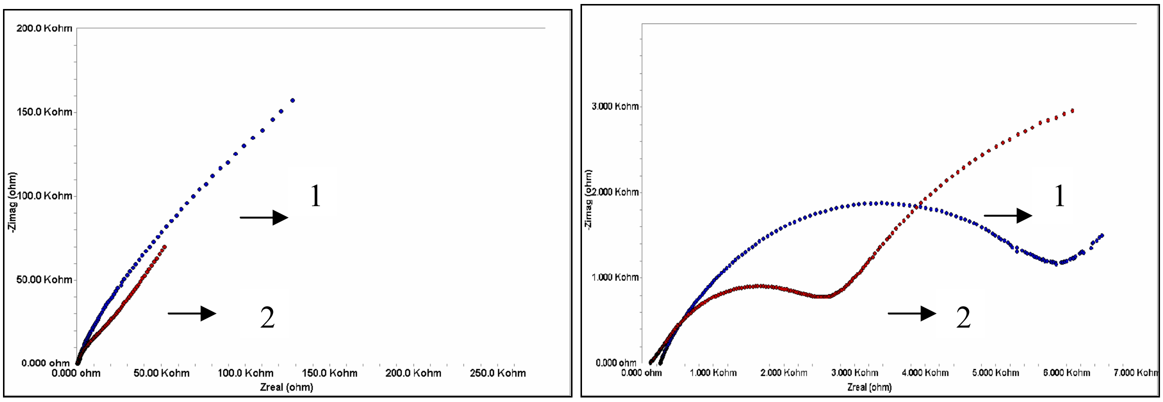


(a) (b)

Figure 2. Open circuit potential of 316L SS obtained in artificial saliva vs time plot: pH=6, T=37,2°C; (a), sintered 316s, (b), casting 316L and natural aeration conditions.

The study reveals that OCP values stabilize with time in the two biomaterials due to spontaneous formation of a passive oxide film. In the first picture (**Figure 2**), the open circuit potential is given by presenting comparison of the corrosion behavior of 316L S and 316L samples after a standard polishing, in the artificial saliva solution. The results show much better performance of the sample sintered.

Electrochemical impedance spectroscopy results were obtained each time after holding the samples at open circuit potential for 60 minutes.



AISI 316L AISI 316S

Figure3. The Nyquist curves of AISI 316L and AISI 316S alloy in artificial saliva, pH=6, at 37,2 °C and different time exposes and natural aeration conditions; (1), t=0 hours, (2), t=120 hours.

Some of the impedance diagrams, obtained for sintered and casting alloys at different potential and time exposure are shown in the **figure 3**. Shapes of the impedance diagrams depended strongly on potential. Diagrams were selected at characteristic regions in such a way to depict clearly the changes of the impedance by changing potential.

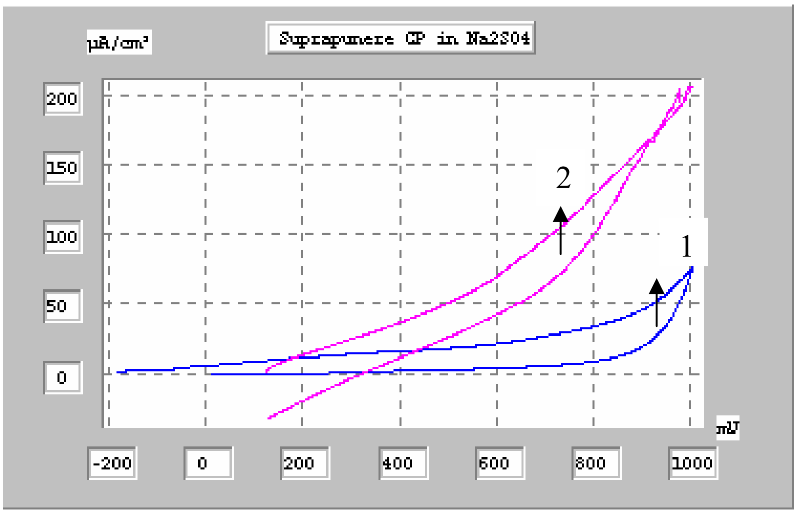


Figure 4. The Polarization curves at 15 mV/min for both alloys (1-AISI 316L and 2-AISI 316S) in Na_2SO_4 0.1M solution at 37,2°, pH=6 and natural aeration conditions.

In **Figure 4**, the polarization curves are presented, showing the electrochemical behavior of AISI 316L and AISI 316S alloys in Na_2SO_4 solution. One may easily observe the best performance of 316L sample.

In the next figure (**figure 5**), the polarization curves show corrosion behavior of AISI 316L and AISI 316S alloys, were obtained in the artificial saliva at pH=6. Here, we also observed the best performance of 316L sample.

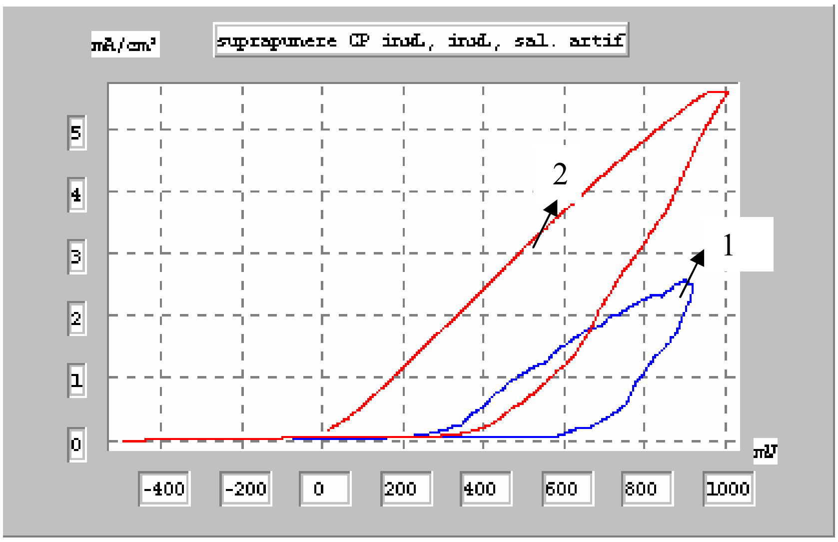
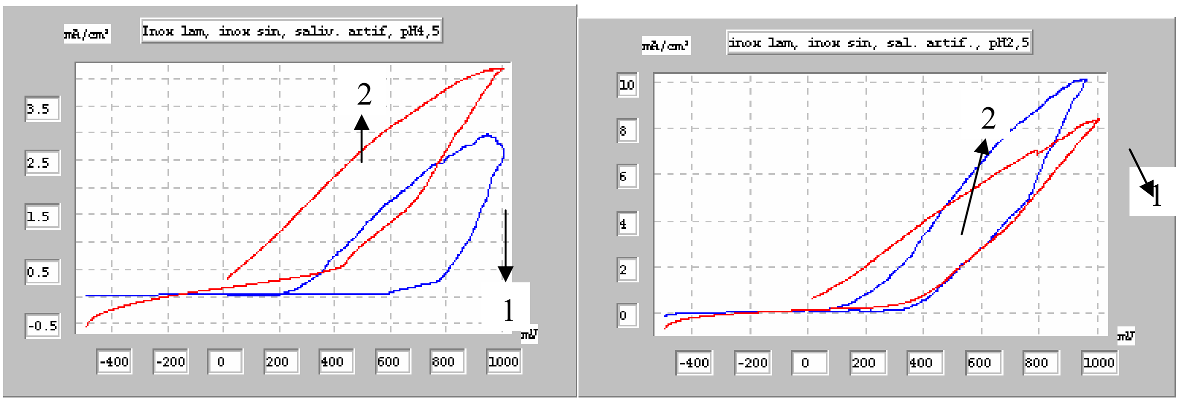


Figure 5. The Polarization curves at 15 mV/min for both alloys (1-AISI 316L and 2-AISI 316S)

in artificial saliva at 37,2°, pH=6 and natural aeration conditions.

The polarization was carried out from –400 mV to 1000 mV (SCE) at a scan rate of 150 mVmin-1 to construct the Tafel plots (logarithmic variation as a function of voltage). The corrosion potential Ecorr and corrosion current Icorr were determined from the intersection of these two linear plots [7]. The electrochemical and corrosion parameters are presented in **table 1** and **2**.



(a) (b)

Figure 6. The Polarization curves at 15 mV/min for both alloys (1-AISI 316L and 2-AISI 316S) in artificial saliva at 37,2°, in natural aeration conditions at pH=4,5(a) and pH=2,5 (b).

Figure 6 presents comparison of polarization curves obtained covering different values of pH solutions. We observe that passivity range for both alloys narrow with the decrease of pH value.

Table 1. The main electrochemical and corrosion parameters of AISI 316L in artificial saliva at 37,2° and natural aeration conditions

Sample	pH	v_{cor} (mm/year)	i_{cor} ($\mu A/cm^2$)	E_{cor} (mVvs. SCE)	R_p (kΩ)
AISI 316L	6	0,013	1,09	-252,4	29,52
	4,5	0,046	3,93	-306,3	23,81
	2,5	0,056	4,80	-288,2	7,48

Table 2. The main electrochemical and corrosion parameters of AISI 316S in artificial saliva at 37,2° and natural aeration conditions

Sample	pH	v_{cor} (mm/year)	i_{cor} ($\mu A/cm^2$)	E_{cor} (mVvs. SCE)	R_p (kΩ)
AISI 316S	6	0,029	2,51	-152,9	18,75
	4,5	0,77	65,8	-175	1,15
	2,5	0,76	64,9	-177	1,46

v_{corr} is corrosion rate calculated from Tafel slopes, mm/y;

R_{p1} from Rp measurements, (kΩ
Icorr is current corrosion calculated from Tafel slopes, μA/cm^2;
E corr is potential corrosion, mVvs SCE.

It appears that the highest value of corrosion rate has been obtained for AISI 316 S sample in artificial saliva at pH=4,5. The corrosion rate increase with the decrease of pH solution and the corrosion potential E_{corr}, remove for negative values.

Metallic biomaterials are normally considered to be highly corrosion resistant, owing to the presence of an extremely thin passive oxide film that spontaneously forms on their surfaces. These films serve as a barrier to corrosion processes in alloy systems that would otherwise experience very high corrosion rates [8]. That is, in the absence of passive films, the driving force for corrosion for typical implant alloys (e.g., titanium-based, cobalt chromium (CoCr)–based, and stainless-steel alloys) is very high, and corrosion rates would also be high. The properties of these passive oxide films depend to a large extent on their structure and chemistry, which are themselves dependent on the substrate's prior thermal, mechanical, and electrochemical history.

Conclusions

This study shows the difference in corrosion behavior of a medical grade AISI 316 stainless steel between casting and sintered biomaterial surfaces.

The obtained results are evident and indicate a better corrosion resistance of AISI 316L by decreased corrosion rate in the artificial saliva, as well as in the aqueous Na_2SO_4 solution. These improvements may have a profound influence on bio- and homeocompatibility of metallic biomaterials.

These aspects argue the possibility of an advantageous use of PM material in applications reserved until now only to the rolled material.

References

1. Gotman I. Characteristics of metals used in implants. J Endourol 1997,11(6), 383–9.
2. Renata Poljak-Guberina et al. Dental Alloys and Corrosion Acta Stomatol Croat, Vol. 36, br. 4, 2002. 448
3. Weiss CM, Weiss A: Principles and Practice of Implant Dentistry, St. Louis, 2001, Mosby Inc., pp.42-45.
4. Cigada A, Rondelli G, Vicentini B, Giacomazzi M, Roos A. Duplex stainless steels for osteosynthesis devices. J Biomed Mater Res 1989, 23, 1087-95.

5. R. A. Lula, and I. M. Bernstein, “ Residual and Minor Elements in Stainless Steels” in Handbook of Stainless Steels, D. Peckner and I. M. Bernstein, editors, McGraw- Hill Book Co., New York, 1977, p. 14-10.
6. Medical Devices, Vol.13.01, Annual Book of ASTM Standards, 1992
7. M. Stern, A. L. Geary, J.Electrochem.Soc, 104, (1957), 56
8. Misch C E, Contemporary Implant Dentistry, ed. 2, St. Louis 1999, Mosby Inc, pp. 286-293