SEM and EDX Study of Stainless Steels, Suggested as Human Body Implants

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Abstract. The most important requirement for any material used as an implant is to be biocompatible and not to cause undesirable effects in the human body. Corrosion of implants is included in the topic of biocompatibility because it is a determining factor in their sustainability and seamless fulfillment of their functional purpose. The work presents the results obtained in the comparative study of two austenitic stainless steels (Cr18Ni9 and Cr18Mn12N) in two models of artificial saliva, accepted as environments for testing the corrosion behavior of materials for these aims. The nature of the corrosion attack, the composition of the corrosion products at 37°C and the pH 5.5 and pH 6.75 of the model media were determined using physical methods such as SEM and EDX of investigation and analysis. It was found that Cr18Mn12N steel (0.61 % N), exhibits higher corrosion resistance.

1. Introduction
Biocompatibility of dental material is a fundamental requirement of successful behavior in oral cavity. It draws on knowledge from biology, patient risk factors, clinical experience and engineering. There are two key factors that appear to be important in determining biocompatibility of any dental material − some involve various types of corrosion or material degradation and others include surface characteristics. Dental materials within the mouth interact continually with physiological fluids.

More often used orthodontic appliances are mainly made of stainless steels, nickel–titanium alloy, titanium and its alloys, or cobalt-chrome alloys, which have high corrosion resistance due to their stable passive films [1]. Later, stainless steel has proven to be a better material than noble metal alloys for orthodontic appliances. This superiority is primarily due to its low cost, greater strength, higher modulus of elasticity, good formability, and high corrosion resistance in the mouth. These advantages have been accepted by orthodontists, and as a result stainless steel is used extensively for bands, brackets, and arch wires [2].

Recently it has become apparent that there are needs for even higher corrosion resistance, high strength, improved formability, and lower cytotoxicity. Much effort has gone into satisfying these needs and into improving the properties of stainless steels. Super stainless steels that have higher corrosion resistances and greater mechanical strengths than the conventionally used stainless steels have been developed and these could overcome disadvantages [3-4].

Corrosion, the degradation of materials by electrochemical attack, is of concern particularly when orthodontic appliances are placed in the hostile electrolytic environment provided by the human mouth [5].

For all practical purposes, the metallic orthodontic wires cannot be isolated electrically from the tooth. Resistance to corrosion is critically important for orthodontic wires because corrosion can lead
to roughening of the surface, weakening of the appliances, and liberation of elements from the metal or alloy. Release of elements can produce discoloration of adjacent soft tissues and allergic reactions in susceptible patients. Corrosion can severely affect the ultimate strength of the material leading to mechanical failure of the orthodontic materials.

Some alloys and metals are resistant to corrosion because of inherent nobility or the formation of a protective surface layer. However, many ions containing oral environment can cause corrosion during long time exposure [6-8].

In the present study the corrosion resistance and character of corrosion attack of two stainless steels Cr18Ni9 and HNS Cr18Mn12N in artificial saliva were investigated by SEM and EDX analyses.

2. Experimental
2.1. Materials and methods
The chemical content of the investigated steels are presented in Table 1.

| Steel          | Cr  | Ni  | Mn  | C   | N   | Si  | P   | S   |
|----------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Cr18Mn12N     | wt.%|     |     |     |     |     |     |     |
|                | 16.50| 0.05| 12.00| 0.04| 0.61| 0.36| 0.011| 0.023|
|                | at.%|     |     |     |     |     |     |     |
|                | 17.07| 0.05| 11.74| 0.16| 2.37| 0.70| 0.02 | 0.005|
| Cr18Ni9       | wt.%|     |     |     |     |     |     |     |
|                | 17.49| 9.37| 1.29 | 0.05|- | 0.52| 0.022| 0.009|
|                | at.%|     |     |     |     |     |     |     |
|                | 18.74| 8.85| 1.23 | 0.23 | | 1.03| 0.04 | 0.016|

The electrochemical treatments of the samples before the surface analyses were conducted in a conventional three electrodes cell in open air conditions at 37°C, with a platinum counter electrode and a saturated calomel electrode (SCE) as a reference one. The experiments were carried out with EG&G Princeton Applied Research, Potentiostat/Galvanostat Model 263A, provided with the specialized software package PowerCORR®. After the anodic polarization for 20 minutes at potential 100 mV more positive than the pitting potential determinate potentiodynamically for each steel in an artificial saliva.

Two physical methods for investigation of the surface were carried out. Scanning electron microscopy (SEM). The morphology and structure of the surfaces were examined by scanning electron microscopy, using a SEM/FIB LYRA I XMU, TESCAN electron microscope, equipped with ultrahigh resolution scanning system secondary electron image (SEI).

Energy dispersive X-ray spectroscopy (EDX). The energy dispersive spectroscopy is a local X-ray spectral analysis which permits qualitative and quantitative determination of surface micro volume contents of the order of several µm³. Apparatus Quantax 200, BRUKER with spectroscopic resolution at Mn-Ka and 1 kcps 126 eV is used.

2.2. Solutions
Two types of artificial saliva, presented in Table 2, are used. The second one is received by modification of the first with 1M HCl to acidify the solution. The parameters pH and σ, mS sm⁻¹ of the solutions are pointed at Table 3.

Table 1. The chemical composition (wt.% and at.%) of the tested stainless steels.

| Solution | Composition of the solution, g l⁻¹ |
|----------|----------------------------------|
| Saliva   | NaCl    | KCl    | CaCl₂·2H₂O | Na₃HPO₄·2H₂O | NaS·9H₂O | Urea, Dist.H₂O |
|          | 0.40    | 0.40   | 0.795      | 0.780        | 0.005    | 1.00          | 1000         |
Table 3. The parameters of the solutions.

| Solution          | pH  | σ, mS cm⁻¹ |
|-------------------|-----|------------|
| Saliva-1          | 6.75| 3.01       |
| Saliva(HCl)-2     | 5.5 | 3.50       |

3. Results and discussions

3.1. SEM – analyses

The main form of corrosion on the steel surfaces after electrochemical treatment of the samples is basically pitting corrosion. In order to establish the type and size of the pits appeared on the surfaces of both investigated steels, the samples were observed by scanning electron microscopy. The microphotographs for both steels are presented on Figure 1 for saliva-1 and on Figure 2 for saliva-2.

The microscopy observations indicate more numerous pits on Cr18Ni9 steel surfaces which are larger in comparison to these on the surface of the Cr18Mn12N samples in both solutions.

The pits occurring at the nitrogen steel surface are spherical in shape and could be divided formally into two groups: small pits with diameters in the rage 20-60 μm and large pits with diameters of about 200 μm.

The pits on the nickel steel surface are also spherical in shape, but in contrast to the nitrogen steel samples they are larger (with 200-250 μm in diameter) and deeper.

Some of the pits are open and the others are under surfaces types.

![Figure 1. SEM microphotographs of (a, b) Cr18Ni9 and (c, d) Cr18Mn12N steels after potentiostatic polarization in saliva-1.](image-url)
Figure 2. SEM microphotographs of (a, b) Cr18Ni9 and (c, d) Cr18Mn12N steels after potentiostatic polarization in saliva-2.

3.2. EDX analyses
EDX analyses of the surfaces on the bottom of the pits were performed after electrochemical treatment of the samples in two solutions: saliva-1 and saliva-2.

| Elements | Concentration  | Concentration  | Concentration  | Concentration  |
|----------|----------------|----------------|----------------|----------------|
|          | Wt. %          | At. %          | Wt. %          | At. %          |
| Fe       | 61.68          | 56.68          | 45.61          | 36.32          |
| Cr       | 18.19          | 17.95          | 15.01          | 12.84          |
| Ni       | 8.87           | 7.76           | -              | -              |
| Na       | -              | -              | 12.33          | 23.86          |
| Mn       | 5.76           | 5.38           | 14.24          | 11.53          |
| O        | 1.48           | 4.75           | -              | -              |
| C        | 0.72           | 3.08           | -              | -              |
| Ti       | 1.48           | 1.59           | -              | -              |

Table 4. EDX analyse of the elements saliva-1.
The analysis of the corrosion products (Table 4 and Table 5) indicates high content of O, P and Cl and other elements, which are components of the solutions, as well as Fe, Mn, Ni, Cr and so on. Therefore, apart from the oxides formation during surface dissolution there exist also metal chlorides and phosphates. The results presented in the tables indicate that the solution saliva-2 more aggressive to investigate steels.

### Table 5. EDX analyse of the elements saliva-2.

| Elements | Concentration Cr18Ni9 | Concentration Cr18Mn12N |
|----------|-----------------------|------------------------|
|          | Wt. % | At. % | Wt. % | At. % |
| Fe       | 40.98 | 22.71 | 40.35 | 31.67 |
| Cr       | 18.57 | 11.05 | 23.89 | 20.14 |
| Ni       | 4.92  | 2.60  | -     | -     |
| Mg       | -     | -     | 1.45  | 2.61  |
| Mn       | -     | -     | 19.35 | 15.44 |
| O        | 16.75 | 32.40 | 7.11  | 19.47 |
| C        | 8.01  | 20.64 | -     | -     |
| Ti       | 1.60  | 1.03  | -     | -     |
| Cl       | 0.90  | 0.78  | 1.81  | 2.24  |
| P        | 1.78  | 1.77  | 0.76  | 1.08  |
| Al       | 3.70  | 4.25  | 2.33  | 3.78  |
| S        | 1.39  | 1.34  | 0.71  | 0.97  |
| Ca       | 0.43  | 0.33  | 1.42  | 1.56  |
| Cu       | -     | -     | 0.26  | 0.18  |
| Si       | 0.98  | 1.08  | 0.55  | 0.86  |

### 4. Conclusions

At the time of comparative investigation the corrosion behavior of two austenitic stainless steels (Cr18Ni9 and HNS Cr18Mn12N), suggested for the orthodontic appliances, in two model artificial saliva were defined the character (pitting corrosion, with different in size spherical pits) and the probable composition of the corrosion products. The results manifested that the nitrogen-containing steel possess higher résistance in model media and hence more suitable for orthodontic appliances.

### 5. References

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