Influence of electrochemical corrosion tests in an artificial environment on the chemical composition of a Co-Cr-Mo dental alloy

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Abstract. The goal of this study consists in the determination of structural modifications produced in a non-noble alloy intended for metal components of the skeletonized removable partial dentures following electrochemical corrosion in artificial saliva. The behavior to electrochemical corrosion was shown by the microstructural and chemical analysis by means of an electron scanning microscope fitted with an EDAX electron detector. We noticed that on the analyzed surface of Co-Cr-Mo alloy (Remanium GM 800, Dentaurum) that the Co and Mo elements lost their initial mass percentage, whereas others like Si increased their mass percentage with a very small quantity, a fact indicating the corrosion of Co and Mo elements and a better resistance of silicon. Following the determinations made, we may affirm that Co-Cr-Mo alloy (Remanium GM 800, Dentaurum) has a behavior to electrochemical corrosion in artificial saliva of generalized type and preferential by phases, with oxidization on the entire surface of the material and the formation of a superficial corrosion layer on the phase of matrix type.

1. Introduction

Co-Cr-Mo alloys proposed for alloys meant for medical uses are in cast and raw state in the first phase complying with the chemical compositions in ASTM standards.

In general, there are two types of Co-Cr-Mo alloys used for biomedical applications: “high carbon” (usually 0.15-0.25 wt%) and “low carbon” (below 0.06 wt%) [1, 2]. Despite all that, both alloys have at least 60 wt% Co. The alloys contain about 28% Cr which forms a thin layer of passive Cr₂O₃ on the metal surface [3-5]. This layer has a high resistance to corrosion through the separation of metal from air and watery media. Usually these alloys contain 5-7 Wt % Mo which is added to improve the mechanical properties of alloys as it forms solid solutions that increase the alloy’s resistance and also increase the local resistance to corrosion [6, 7]. The alloy exhibits a layer of oxide on the surface that forms a thin passivating film that has an enriched percentage of chrome. Following the tests, it is noticed that a 1-4 µm thick layer of oxide is formed having a very high resistance to corrosion [8-13].

The fundamental approach of the electrochemical corrosion phenomenon must take into account the alloy nature and structure, the nature of the environment and the reactions occurring at the alloy-environment interface [14].
The goal of this study consists in the determination of the structural modifications produced within a Co-Cr-Mo alloy for metal components of the skeletonized removable partial dentures following electrochemical corrosion in Afnor artificial saliva.

2. Materials and methods
For the experimental researches we made specimens of cylinder shape from Co-Cr-Mo alloy (Remanium GM 800, Dentaurum) that were mounted on teflon holders.

The corrosion tests were carried out in a solution of AFNOR artificial saliva. The pH characteristic was measured by means of a multi-parameter analyser of CONSORT 831C type and the actual pH value of Afnor saliva was 6.7.

The specimens prepared this way were analysed structurally and chemically. For this purpose we used a scanning electron microscope fitted with an EDAX electron detector. Then, they were subjected to the electrochemical corrosion tests in Afnor artificial saliva. To identify the structural and chemical modifications occurred within the Co-Cr-Mo alloy following the corrosion process, we repeated the electron microscopy and chemical analysis tests.

3. Results and discussions
In figure 1 we present the specter of energies characteristic to Co-Cr-Mo alloy and the identification of the chemical elements Co (x2), Cr (x1), Mo (x3) and Si (x1) participating to the alloy with diverse energies specific to the different chemical bonds they make.

![Figure 1. Specter of energies characteristic to the elements identified qualitatively on the surface of Co-Cr-Mo alloy (Remanium GM 800, Dentaurum).](image)

The chemical elements determined quantitatively through EDS technique fit into the ones given by the characteristic standard by also taking into consideration the standard error of the equipment. In table 1, we present the chemical composition of Co-Cr-Mo alloy in wt.% and at.%.

| Element | Percentage values | Standard error % |
|---------|-------------------|------------------|
| Co      | 61.62             | 60.33            | 1.41             |
| Cr      | 29.15             | 32.34            | 0.71             |
| Mo      | 8.01              | 4.81             | 0.45             |
| Si      | 1.22              | 2.51             | 0.09             |
The phase analysis and chemical compositions were carried out in three distinct points of the surface of metal specimens (figure 2):
- Point 1: on the limit of grains of alloyed solid solution;
- Point 2: inside the solid solution grains (matrix);
- Point 3: at the level of a crack.

**Figure 2.** Surface of Co-Cr-Mo alloy (Remanium GM 800, Dentaurum) and the points where the chemical tests were performed.

**Figure 3.** Specter of energies characteristic to the elements identified on the surface of Co-Cr-Mo alloy (Remanium GM 800, Dentaurum) corroded alloy and in detail the specter for point 3 in figure 2 where energy lines may be seen for C and P.

The presence of high Cr content caused the formation of carbides M23C6 and M3C2 distributed in the austenitic matrix with a favourable effect on the resistance to corrosion in the artificial saliva environment. Mo hardens the alloyed solid solution F (A) and contributes to the finishing of microstructure.

The elements identified quantitatively by spectroscopy of dispersive energies (figure 3) are quantified in table 2.

**Table 2.** Chemical compositions obtained for the surface in figure 2 for the entire surface (the chemical analysis was made on a 2500 µm² surface) and in the points marked on the image (the chemical analysis was made of a 90 nm spot).

| Chem. elem./ area | Co wt % | Co at % | Cr wt % | Cr at % | O wt % | O at % | Mo wt % | Mo at % | Si wt % | Si at % | C wt % | C at % | P wt % | P at % |
|-------------------|---------|---------|---------|---------|--------|--------|---------|---------|--------|--------|-------|--------|-------|--------|
| Surface           | 47.5    | 33.1    | 29.1    | 22.9    | 14.8   | 38.04  | 6.4     | 2.7     | 2.1    | 3.1    | -     | -      | -     | -      |
| Point 1           | 30.1    | 18.5    | 35.8    | 25.01   | 16.7   | 37.8   | 12.8    | 4.9     | -      | -      | 4.6   | 13.8   | -     | -      |
| Point 2           | 46.8    | 29.4    | 26.2    | 18.7    | 16.9   | 39.3   | 5.7     | 2.2     | 1.8    | 2.8    | 2.6   | 8.02   | -     | -      |
| Point 3           | 43.9    | 26.1    | 25.4    | 17.1    | 19.9   | 43.7   | 5.3     | 1.9     | 2.1    | 2.7    | 2.7   | 7.9    | 0.6   | 0.63   |
| EDAX err.         | 1.1     | 0.6     | 2.8     | 0.4     | 0.1    | 0.5    | 0.2     |         |        |        |       |        |       |        |

The experimental results indicate major differences between the values of initial chemical compositions and the ones registered after running the electrochemical corrosion tests. Besides the variations of percentage quantities of different chemical elements, we may also notice their migration trends among the three points under analysis.

The chemical analysis performed in points 1 and 2 shows the Co migration towards the center of the solid solution grains, while Cr and Mo migrate towards their limit and have a homogenous quantitative distribution. The reduction of C concentration is due to the process of carbide formation with preferential arrangement towards points 2 and 3. Important is the presence of O at the level of entire surface, a fact indicating the presence of a general oxidation process much more intense at the level of point 3.
In figure 4 we present the analysis of distribution of the chemical elements Co, Cr, Mo, C, Si, O, P: on the line selected in figure a) and the variations of elements in b) with details of element variations having a lower signal in c).

Figure 4. Analysis of distribution of the chemical elements Co, Cr, Mo, C, Si, O, P: a) the selected line, b) the variations of elements, c) details of element variations having a lower signal.

The selected line totally crosses the structure of the investigated surface, the results of chemical composition tests and the presence of a general oxidation process being confirmed.

Figure 5 presents the analysis of the distribution of Co, Cr, Mo, C, Si, P and O elements on the selected area a), simultaneously for all elements in b) and individually for each element in c)-i).

Figure 5. Analysis of the distribution of Co, Cr, Mo, C, Si, P and O elements on the selected area a), simultaneously for all elements in b) and individually for each element in c)-i).
The manner of distribution of the chemical elements on the selected area is in concordance with the results of chemical composition tests, their migration trends between the limits and the centre of crystalline grains being highlighted.

The corrosion of Co-Cr-Mo alloy (Remanium GM 800, Dentaurum) is of a generalized type and preferentially by phases with the oxidization of the entire surface of the material and the formation of a superficial layer of corrosion on the phase of matrix type.

4. Conclusions

By using the SEM and EDS analysis techniques, we investigated the surface of Co-Cr-Mo alloy (Remanium GM 800, Dentaurum) after it was subjected to an electrochemical corrosion test on potentiostat equipment in a solution of AFNOR artificial saliva.

The alloy under analysis corroded more intensely in the phase of metal matrix type by forming a 2-3 µm layer of oxide and also in the dendritic phase exhibiting a thin oxide layer. After polishing, Co-Cr-Mo alloy (Remanium GM 800, Dentaurum) showed a surface with small variations between phases but with variations that got more pronounced after the electrochemical corrosion test.

On the analysed surface of Co-Cr-Mo alloy (Remanium GM 800, Dentaurum) we could see that the Co and Mo elements lost some of their initial mass percent, while others such as Si increased their mass percent with a very little quantity, a fact indicating a corrosion of Co and Mo elements and a better resistance of the silicon. As compared to the initial surface, Cr maintained its mass percent. To compensate for the lost percent of Co and Mo, O appeared in a high percentage while C and P appeared in some areas.

Following the determinations made, we may affirm that Co-Cr-Mo dental alloy (Remanium GM 800, Dentaurum) has a behavior to electrochemical corrosion in artificial saliva of generalized type and preferentially by phases, with oxidization on the entire surface of the material and the formation of a superficial layer of corrosion in the phase of matrix type.

5. References

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