Influence of pH on the Corrosion Behaviour of Laser-Processed Co-Cr Dental Alloys in Artificial Saliva

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Abstract. The materials used in dental restorations must present, aside from a mechanically stable and fracture resistant structure and a high level of biocompatibility, a strong resistance towards corrosion over a wide range of pH values. This research focuses on the relation between two different CAD-manufacturing procedures of base Co-Cr alloys used in dental restorations regarding the assessment of their corrosion resistance in artificial saliva at various pH levels. We comparatively appraised the corrosion behaviour of two cobalt-chromium dental alloys manufactured by two alternative computer assisted technologies namely selective laser melting (SLM) and selective laser sintering (SLS). Several electroanalytical techniques like linear polarization, cyclic voltammetry and electrochemical impedance spectroscopy have been employed to study the processes taking place at the metal/electrolyte interface. Preliminary results reveal that computer assisted processing technologies could represent an alternative when considering the manufacture of complex restorations.

1. Introduction

The oral cavity represents an extremely complex and ever changing environment implying moisture, large temperature variations that can range from about 5°C while consuming cold fluids or ice cream to more than 55°C during the intake of hot meals, coffee or tea, relatively high forces during mastication as well as a substantial pH variation. In healthy individuals, saliva has a complex composition based mainly on water soluble electrolytes, proteins, hormones, as well as bacteria while it's pH is very close to neutral, having values of about 6.7 to 7.4 [1, 2]. These values can dramatically change due to various physical conditions like gastroesophageal reflux disease, drug intake, consumption of citric fruits or juices. All these factors require that the materials used in dental restorations must present, aside from a mechanically stable and fracture resistant structure and a high level of biocompatibility, a strong resistance towards corrosion over a wide range of pH values.

The most important categories of materials used in dentistry are represented by ceramics, polymers, composites and metals/alloys [3]. The aforementioned material clusters find their use mainly for dental prostheses as well as restorations. Many of the new computer aided technologies used for the fabrication of metallic structures implemented in the last decade can be divided into two major classes based on the treatment of the base material. While milling of pre-processed starting materials falls in the category of subtractive manufacturing, the more recently presented selective laser melting (SLM) and selective laser sintering (SLS) techniques are seen as additive processing technologies [4]. The present research focuses...
on the investigation of the corrosion behaviour of two Co-Cr alloys produced using the latter fabrication methods, within Fusayama artificial saliva by means of specific electroanalytical methods. The pH values used in this investigation ranged from 2.5 to 6.5 with the aim of closely simulating the various physiological conditions to which the restoration material could be exposed.

Base Co-Cr alloys are widely used for manufacturing removable partial dentures, dental crowns, fixed as well as removable prostheses, due to their high strength, excellent resistance to wear, and nonetheless their reasonable price [5]. The traditional casting technology used for over a century for obtaining structures used in dental restorations, has been proven to be extremely time-consuming and labour-intensive. It has proven its limitations while machining advanced designed parts [6]. That is the reason why new additive manufacturing technologies made their way in prosthetic dentistry, gaining popularity due to higher precision and speed, compared to traditional casting methods. New additive manufacturing techniques are mainly processes that conjunct computer aided design to a high intensity laser beam with the purpose to gradually melt (or sinter) the metallic powder used as raw material, resulting in complex and relatively dense final products. The technology not only delivers very accurate manufacturing, but could significantly reduce production costs [7]. The mentioned Laser based processing technologies known as Selective Laser Sintering (SLS) and Selective Laser Melting (SLM) are currently employed to produce dental restoration devices. A high power laser is used to partially (SLS) or fully (SLM) melt a metal powder to form specific complex shaped objects. Even though comprehensive studies of the biocompatibility of Co-Cr dental alloys have been conducted, it is well known that the engaged processing technology can highly influence the surface microstructure and in consequence corrosion behaviour and thus biocompatibility [8].

The complex electrolyte environment found in the oral cavity is subjected to multiple changes regarding parameters such as temperature, humidity, pH and composition, all of these can induce corrosion and thus damage to dental alloys, hence affecting their biocompatibility [9, 10]. The existence of narrow interproximal spaces, where food and plaque generated by microorganisms can accumulate in the vicinity of dental restorations may create more acidic conditions that, in turn, can facilitate corrosive reactions [11]. Corrosion of these medical devices may lead to metal ions originating from the base alloy being released into the body. These ions can travel to different body regions through the digestive passage, lungs and oral tissues exerting toxic as well as allergic reactions [12]. This is why the in-depth knowledge of the mechanisms governing the corrosion processes affecting the above mentioned alloys is of paramount importance.

The present study aims to elucidate the corrosion mechanisms of the studied alloys at different acidity levels of the medium in order to further improve the employed manufacturing techniques towards reducing potential harmful agents that could be released during long term use, thus making them less prone to locally or systemically occurring adverse reactions.

2. Experimental
Samples of cylindrical shape with the diameter of 10 mm and the height of 2 mm have been obtained through two distinct machining processes, namely: the CAD selective laser sintering technique using a commercial Co-Cr base material and the CAD selective laser melting technology using Co-Cr powder. The chemical composition of the investigated probes, as given by the manufacturer, is detailed in Table 1. After cooling down, the probes have been air-blasted with alumina particles and mechanically finished and polished using specific techniques. Oxide-firing (at 950 – 980°C) was undertaken, as required for porcelain veneering for both samples, the metal surface was finally blasted with aluminium oxide (75 μm).

All electrodes obtained as above were finished using silicon carbide and 1μm grit diamond paste respectively, degreased and treated ultrasonically in distilled water, rinsed and dried prior to be subjected to electrochemical investigations. Electrochemical investigations have been undertaken using a BioLogic SP150 potentiostat/ galvanostat along with a conventional three-electrode cell system. All electrochemical measurements have been undertaken using Fusayama artificial saliva as electrolyte solution [13]. Electrochemical impedance spectroscopy (EIS) investigations have been conducted using
a BioLog SP150 potentiostat/galvanostat equipped with an EIS module, within the frequency between 100 kHz and 10 MHz. The amplitude of the alternating voltage was of 10 mV. A number of 60 points have been recorded for each spectrum with a logarithmic distribution of 10 points per decade. The experimental data has been fitted using the ZView – Scribner Associates Inc. software and equivalent electrical circuits by applying the Levenberg–Marquardt least squares complex non-linear fitting algorithm [14].

| Probe | Co | Cr | Mo | Mn | W | Si | Fe | C |
|-------|----|----|----|----|---|----|----|---|
| SLS   | 59 | 25 | 3.5| <1.5| 9.5| <1 | <1.5| <1.5|
| SLM   | 59 | 25 | 3.5| <1.5| 9.5| <1 | <1.5| <1.5|

3. Results and Discussion

The protecting layer coating the majority of the base alloys used in dental restorations is a key factor in inhibiting the release of toxic metal ions in the human body. In order to closely re-create the various situations found in the oral cavity in terms of acidity, we have comparatively studied the corrosion behaviour of two samples fabricated using new CAD assisted technologies, on the basis of a Co-Cr alloy.

The linear polarization curves (Tafel plots) of the samples obtained through selective laser melting (SLM) and selective laser sintering (SLS) in Fusayama artificial saliva electrolyte at acidity levels varying from pH 2.5 to 6.5 are depicted in Figure 1.

![Figure 1. Tafel polarization curves recorded for the SLM (a) and SLS (b) samples in artificial saliva electrolyte at 25°C and various pH values at a scan rate of 1 mV·s⁻¹](image)

The investigated samples exhibit, as expected, very similar corrosion behaviours in the studied media, but nevertheless, some important differences do occur. In the case of the laser melted sample (SLM), the Tafel plot (Fig. 1a) exhibits a strong current increase at potentials lower than 45 mV, most probably due to the reduction of physically dissolved oxygen or the reduction of H⁺ ions, taking into account that the artificial saliva solution was in permanent contact to atmospheric oxygen. Scanning towards more positive potentials reveals the transition region between the cathodic and the anodic field characterized by a sudden decrease of the current density at potentials around -0.2 V. It is to be pointed out that the corrosion potential of the studied sample (Ecorr) shifted towards more negative values with increasing pH, while the corrosion current density (icorr) increased significantly with increasing acidity of the medium. At potentials beyond Ecorr a relatively large passive region is revealed, with slowly growing currents over no a potential range up to about 1.0 V. No transpassive behaviour has been
recorded under these circumstances within the studied electrochemical window, revealing that the metal oxides formed during passivation are adherent and have a highly protective character, as confirmed by other studies in the field [15].

The potentiodynamic characteristics of the sintered probe (Fig. 1b) are highly similar in shape, but closer analysis reveals that in the latter case the magnitude of the corrosion currents is slightly higher. The corrosion potentials shift towards more negative values with acidity increase, suggesting a direct influence of the medium on the corrosion kinetics. However all potentials are situated at more anodic levels compared to the SLM sample which could be an indication for a slightly higher corrosion affinity. The transpassive region, characteristic for the breakdown of the passive coating, does not come up, leading to the assumption that the formed film is kinetically stable on the studied potential domain.

Specific Tafel parameters like corrosion rate ($i_{corr}$), and corrosion potential ($E_{corr}$), polarization resistance ($R_p$), corrosion current density ($i_{corr}$), computed for each sample at different values of solution pH are listed in Table 2. The data shows that, the corrosion potential in the case of the SLM sample varies negatively with increasing pH, while the laser sintered (SLS) probe exhibits quite the opposite behaviour, with the most negative corrosion potential recorded at the most acidic pH. The corrosion rate however, is of the same order of magnitude in both samples and remains the highest in the medium with the lowest pH.

| Sample | pH  | $i_{corr}$ [μA cm$^{-2}$] | $E_{corr}$ [mV] | $-b_c$ [mV dec$^{-1}$] | $b_a$ [mV dec$^{-1}$] | $R_p$ [kΩ] | $v_{corr}$ $\times 10^3$ [mm year$^{-1}$] |
|--------|-----|--------------------------|----------------|--------------------------|--------------------------|------------|----------------------------------|
| SLM    | 2.5 | 0.63                     | -194           | 458                      | 232                      | 26.2       | 8.56                             |
|        | 3.5 | 0.50                     | -206           | 466                      | 225                      | 38.2       | 6.79                             |
|        | 4.5 | 0.41                     | -214           | 476                      | 212                      | 41.7       | 5.58                             |
|        | 5.5 | 0.33                     | -222           | 481                      | 198                      | 51.5       | 4.52                             |
|        | 6.5 | 0.24                     | -231           | 430                      | 188                      | 62.3       | 3.24                             |
| SLS    | 2.5 | 0.68                     | -219           | 385                      | 187                      | 23.4       | 9.17                             |
|        | 3.5 | 0.57                     | -210           | 379                      | 182                      | 32.2       | 7.69                             |
|        | 4.5 | 0.45                     | -196           | 374                      | 171                      | 38.7       | 6.09                             |
|        | 5.5 | 0.36                     | -187           | 343                      | 165                      | 49.1       | 4.91                             |
|        | 6.5 | 0.26                     | -175           | 309                      | 145                      | 60.8       | 3.49                             |

A more in-depth investigation to further clarify the corrosion processes taking place at the alloy-solution interface for both probes implies cyclic voltammetry experiments in artificial saliva at two pH values at a scan speed of 100 mV s$^{-1}$. The potential window covered a relatively wide potential domain, reaching from a cathodic value of -1.5 V, up to an anodic switching potential of +1.5 V. Figure 2a) depicts the cyclic voltammograms recorded on an electrode obtained through the SLS technique, at pH values of 2.5 and 6.5 respectively. Scanning from the open circuit potential towards positive values reveals a single, relatively broad anodic peak. The peak height recorded at pH 2.5 is about 4.8 A m$^{-2}$ whereas the pH increase leads to a pronounced lowering of the current signal, the value dropping to about only 2.5 A m$^{-2}$. The increase of the peak height at more acidic values can be an indication for a rate increase of the studied corrosion process, possibly due to the breakdown of the passive film formed at the electrode surface. Finally, at more positive values, the oxygen evolution process triggers a sharp increase of the current density.

Switching the scan direction towards negative potentials reveals a weak cathodic signal at potentials of about +0.25 V in both media, probably due to the reduction of adsorbed oxygen at the electrode surface, followed by a quite large passive region in both media, with no detectable signals up to the potential at which the hydrogen evolution reaction causes a swift current increase at potentials starting.
with -0.75 V. As expected, the oxygen and hydrogen evolution processes are highly influenced by the pH of the medium, both shifting towards more negative values with increasing acidity.

The superimposed voltammograms of the two samples, namely SLM and SLS, recorded in highly acidic artificial saliva of pH 2.5 at the same sweep rate of 100 mV s⁻¹ are suggestively depicted in Fig.2b. Although the shapes of the current-voltage dependencies exhibit very resembling characteristics, indicating that the corrosion mechanisms on the two investigated electrode materials might follow similar patterns, there is one difference that strikes the eye. While the peak height corresponding to the sintered Co-Cr alloy (SLS) is about 4.8 A m⁻², the same peak recorded under the same conditions on the laser melted (SLM) electrode is with about 0.4 A m⁻² shorter.

![Figure 2](image_url)

**Figure 2.** Cyclic voltammograms recorded in Fusayama artificial saliva electrolyte at a scan rate of 100 mV s⁻¹ on (a) SLS sample at pH 2.5 and 6.5 and (b) SLS and SLM samples at pH 2.5

This may be an indication for a slight increase of the corrosion processes taking place on the sintered sample. On the SLS electrode, the potential window is characterized by a cathodic shift of the potential at which oxygen evolution occurs. The hydrogen evolution reaction occurs at more positive potentials on the SLS electrode as compared to the SLM probe. Both aforementioned differences may denote a weak catalytic influence of the electrode material over the two processes.

Chronoamperometric investigations on both SLS and SLM samples have been recorded in artificial saliva at various pH, as presented in Fig.3, with the aim of an intrinsic elucidation of the corrosion properties of the studied samples.

Applying a similar constant potential of +250 mV vs. $E_{corr}$ for both, SLS as well as SLM manufactured electrodes and recording the variation of the current density over a timeframe of 15 minutes on the whole array of pH values reveals some new insights regarding the investigated processes. After an initial swift decrease of the corresponding current densities, both samples exhibit an almost constant throughput but there are some mentionable differences. While the SLS sample shows an expectable corrosion behaviour in terms of higher current densities at lower pH, indicating that the more aggressive the medium, the faster the corrosion rate becomes, in the case of the laser melted probe, the transition towards lower current in the case of the pH 5.5 solution occurs only after about 300 seconds after applying the potential step. In the latter case, the different slopes of the constant current region at pH 4.5 and 5.5 respectively, suggest a kinetic hindrance of the investigated processes. The data listed in Table 3 display distinctively higher corrosion current densities recorded for the samples machined by laser sintering compared to those obtained by the laser melting technique, suggesting that the base alloys obtained by the former technology might not efficiently develop a protective and compact passive coating.
Figure 3. Chronoamperometric measurements recorded at +250 mV vs. $E_{\text{corr}}$, for the anodic oxidation of SLS (a) and SLM (b) electrodes in artificial saliva electrolyte at various pH for 15 min.

Table 3. Chronoamperometric data for SLS and SLM samples at +250 mV vs. $E_{\text{corr}}$ in artificial saliva electrolyte at different pH values

| pH  | Sample | $i_{\text{oxidation}}$ [mA m$^{-2}$] | Sample | $i_{\text{oxidation}}$ [mA m$^{-2}$] |
|-----|--------|-------------------------------------|--------|-------------------------------------|
| 2.5 | SLS    | 86                                  | SLM    | 43                                  |
| 3.5 | SLS    | 73                                  | SLM    | 33                                  |
| 4.5 | SLS    | 62                                  | SLM    | 28                                  |
| 5.5 | SLS    | 46                                  | SLM    | 20                                  |
| 6.5 | SLS    | 30                                  | SLM    | 13                                  |

Electrochemical impedance spectroscopy (EIS), has been employed to get further information regarding the passive film formation as well as the corrosion behaviour of the Co-Cr specimens obtained through CAD aided laser melting (SLM) and laser sintering (SLS) respectively, at the pH values of interest. The obtained results are depicted in Figs. 4 and 5 as Nyquist as well as Bode plots for SLM and SLS specimens respectively.

Figure 4. Nyquist (a) and Bode plots (b) recorded at corrosion potentials on SLM samples in artificial saliva electrolyte at different pH values.
The metal/electrolyte boundary can be considered as corresponding to an electrical circuit, as a combination of electronic components. The estimation of the obtained EIS data is generally based on an equivalent electrical circuit (EEC), used in order to characterize the processes occurring at the outer layer of the investigated dental alloys. The results have been evaluated and fitted using an EEC as presented in Fig. 6. The presented circuit uses a series combination of the uncompensated solution resistance, $R_s$, combined with two ($CPE-R$) parallel combinations, each one composed of a constant phase element ($CPE$) and a charge transfer resistance, $R$ [16, 17].

![Figure 5. Nyquist (a) and Bode plots (b) recorded at corrosion potentials on SLS samples in artificial saliva at different pH values](image)

**Figure 5.** Nyquist (a) and Bode plots (b) recorded at corrosion potentials on SLS samples in artificial saliva at different pH values

The constant phase element ($CPE$) was placed into the circuit instead of a pure capacitance. It is a non-ideal capacitor used for the characterization of real electrochemical systems taking into account that the passive films at the electrode surface usually shows specific defects and imperfections [18]. This element accounts more precisely for the processes that take place at the electrode/electrolyte interface. The impedance of the $CPE$ element is given by Equation (1):

$$Z_{CPE} = \frac{1}{T(j\omega)^n}$$

in which $T$ is a parameter that is contingent to the capacity of the double layer, $n$ is an exponent ranged between 0 and 1 which describes the $CPE$ angle.

It has been shown that the corrosion processes taking place at the interface between the studied Co-Cr dental alloys and artificial saliva, imply the formation and growth of an adhering passive coating consisting of several types of metal oxides [19]. The physical correspondence of the EEC displayed in Fig. 6 consists of the association of the alloy/electrolyte interface ($CPE_{alR_e}$) and the passive coating/electrolyte interface ($CPE_{coatR_{coat}}$) [17].
The computed results obtained after fitting are depicted as solid lines in Figs. 4 and 5, while the individual points represent the measured data. Calculated parameters for the elements comprising the EEC are detailed in Table 4 corresponding to the corrosion process of dental alloys obtained through the SLM and SLS technologies respectively, in artificial saliva. The values of the double layer capacity have also been calculated.

**Table 4.** Calculated values of the EEC elements for the corrosion process of SLM and SLS samples in artificial saliva

| Sample | pH | $R_e$ [$\Omega$ cm$^2$] | $T \cdot 10^3$ [F cm$^{-2}$ s$^{-1}$] | $n$ | $R_{coat}$ [k$\Omega$ cm$^2$] | $T \cdot 10^4$ [F cm$^{-2}$ s$^{-1}$] | $n$ | $R_{cl}$ [k$\Omega$ cm$^2$] | $C_{dl} \cdot 10^4$ [F cm$^{-2}$] | $\text{Chi}^2 \cdot 10^1$ |
|--------|----|----------------|----------------|----|----------------|----------------|----|----------------|----------------|----------------|
| SLM    | 6.5 | 21.7 | 2.49 | 0.85 | 3.42 | 0.87 | 0.68 | 147 | 2.77 | 1.36 |
|        | 5.5 | 22.1 | 2.20 | 0.83 | 3.27 | 0.99 | 0.65 | 130 | 3.85 | 1.17 |
|        | 4.5 | 23.1 | 1.90 | 0.81 | 2.88 | 1.05 | 0.62 | 117 | 4.66 | 1.56 |
|        | 3.5 | 23.3 | 1.61 | 0.79 | 2.51 | 1.10 | 0.60 | 101 | 5.50 | 1.64 |
|        | 2.5 | 24.0 | 1.44 | 0.78 | 2.25 | 1.19 | 0.58 | 87.6 | 6.38 | 0.75 |
| SLS    | 6.5 | 30.3 | 3.02 | 0.82 | 2.70 | 1.20 | 0.62 | 61.7 | 4.03 | 3.37 |
|        | 5.5 | 33.4 | 2.57 | 0.81 | 2.35 | 1.24 | 0.61 | 56.5 | 4.42 | 3.78 |
|        | 4.5 | 34.6 | 2.12 | 0.80 | 2.05 | 1.30 | 0.58 | 53.4 | 5.40 | 4.86 |
|        | 3.5 | 34.2 | 2.10 | 0.79 | 1.71 | 1.32 | 0.54 | 50.9 | 6.56 | 4.01 |
|        | 2.5 | 31.2 | 1.70 | 0.77 | 1.39 | 1.42 | 0.52 | 47.1 | 7.88 | 1.76 |

Highly similar shapes of the electrochemical impedance spectra displayed in Figs. 4 and 5, as well as the utilization of the same equivalent circuit shown in Fig. 6, used in order to accurately fit the experimental data obtained for the Co-Cr samples finished through laser melting (SLM) and laser sintering (SLS) in artificial saliva, is suggestive evidence that the processes taking place at the metal/electrolyte interface follow the same pattern, namely the coating of the metal surface with a passive oxide layer [20].

The values of for chi-square at an order of magnitude of $10^3$ are an indication for a highly accurate correlation between the experimental data and the EEC model parameters [21]. Both specimens show $R_e$ values of the order of $10^6$ k$\Omega$ cm$^2$ over the whole array of studied pH values, suggesting that the high corrosion resistances [17] are a result of a compact layer coating the whole exposed surface and thus kinetically hindering oxidation processes that could cause corrosion of the base alloy.

As expected, corrosion resistance of both specimens follows a descending pattern along with the rise of the solution acidity. The charge transfer resistance, $R_{cl}$, that characterizes the dental alloy/electrolyte interface is inversely related to the corrosion rate, i.e., the higher the resistance, the slower the process of corrosion gets, hence the base material is more resistant towards corrosion in the given medium. Twice as big $R_{cl}$ values exhibited by the laser melted samples (SLM) compared to SLS suggest a higher corrosion resistance of the former obtained alloy. High values, of about $10^3$ $\Omega$, of the charge transfer resistance $R_{coat}$, that quantifies the formation of the oxide layer on the alloy surface are an indication of a strong adhesion of the formed oxide film, while protecting efficiently against the ongoing corrosion processes. These values, being significantly higher for the SLM specimen, come to confirm the better corrosion resistance of the latter. All of the above, corroborated to the greater values of the double layer capacity $C_{dl}$ calculated in the case of the laser melted probe come to further validate the higher degree of protection conferred by the passive coating in the latter case.

**4. Conclusion**

The studied Co-Cr dental alloys manufactured by CAD-aided laser melting and laser sintering exhibit, as expected, fairly similar electrochemical responses while studied in artificial saliva with variable acidity. The attempted electrochemical studies revealed satisfying corrosion inhibition offered by the passive coating formed on the alloy surface. A noteworthy difference lies in the higher degree of
resistance towards corrosion exhibited by the Co-Cr alloy manufactured using the selective laser melting technology in Fusayama artificial saliva as compared to the laser sintered specimen. The corrosion rate varied towards higher values with increasing acidity in both cases. The higher corrosion resistance exhibited by the SLM specimen over the entire range of pH values between 2.5 and 6.5 comes varied towards higher values with increasing acidity in both cases. The coating of the alloy surface with a compact passive oxide layer, kinetically hindering further corrosion phenomena was outlined and elucidated by electrochemical impedance spectroscopy. The growth of the protecting layer being favoured on the surface of the SLM sample results in a greater protection thus a higher resistance towards corrosion of the probe crafted by laser melting.

5. References

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