

Comparative Study on the Corrosion Resistance of CAD/CAM and Conventional Processed Co-Cr Dental Alloys in NaCl Solutions

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Abstract. The present study emphasizes on the structural implications of the machining procedure on base Co-Cr dental alloys in terms of corrosion resistance. We comparatively assessed the corrosion behaviour of two cobalt-chromium dental alloys: one manufactured by alternative computer assisted technologies obtained by CAD/CAM milling (MIL) and the other one by conventional melting- casting technology (CAS) in NaCl solutions. The samples have been evaluated using several electroanalytical techniques like: linear polarization, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS). Preliminary testing is showing that the new computer assisted processing technologies are comprised as a viable alternative towards traditional manufacturing methods.

1. Introduction

The most common categories of dental materials are composite materials, ceramics, polymers and various metal alloys [1]. Many of these compounds are used in modern dentistry as parts of various medical devices with the aim of re-establishing the physical as well as the aesthetical condition of the patient [2]. Dental materials based on Co-Cr alloys are widely employed in several restoration techniques because of their resistance towards corrosive agents and their remarkable mechanical characteristics [3]. The obtained structures mounted in the oral cavity, are constantly exposed to an environment with a plethora of dynamically changing physical and chemical parameters. Temperature variations, fluctuations of the oral pH, various electrolytes originating from food or fluid intake as well as from specific medical treatments and physical conditions of the patient as well as bacteria, exert a high level of strain on the used materials [4] leading to corrosion phenomena taking place at the surface of dental alloys in direct contact with the oral tissue. The recently introduced computer aided technology (CAD/CAM) differs fundamentally from the classical manufacturing methods in terms of time efficiency as well as final restoration quality [5] this makes the final products to behave contrastingly towards corrosion compared to the classically obtained samples.

The casting technique of cobalt-chromium (Co-Cr) dental alloys has been used for decades to produce dental restorations [6]. Alternatively, dental alloys can be processed using CAD/CAM technology, as hard or soft milling [7]. Co-Cr alloys exhibit elevated melting points, a greater hardness and relatively lower ductility compared to other noble alloys, which makes them more difficult to process [8]. The hard milling technique offers the advantage of machining industrial prefabricated



blanks without the characteristic casting defects and/or porosities [8]. The microstructure morphology of the Co-Cr alloy varies depending on the used manufacturing technique hence interfacial, chemical as well as mechanical properties are associated as well with the employed processing technology of the base material.

Although various studies were conducted over the years regarding the biocompatibility of various dental alloys, no consensus has yet been reached on this issue. Corrosion behavior of the metal compositions represents a key factor concerning the immunological response towards dental alloys. Metal ions released in surrounding tissues can induce cytotoxicity with apoptosis (cell death), allergic reactions, inflammation and discoloration [9]. Dental restorations residing in the oral cavity are permanently exposed to an ever changing complex environment with fluctuating physical and chemical parameters like temperature variations, shifting of the oral pH value, various electrolytes originating from food or fluid intake as well as from certain medications. All of the above together with the naturally forming of bacterial plaque that could come in contact with the base material, provide ideal conditions for the occurrence of degradation phenomena at the metal surface, thus its partial biodegradation [10-12].

The corrosion resistance of Co-Cr dental alloys is influenced by numerous factors, the most significant being: chemical composition, microstructure and manufacturing technique [10-12]. Considering the relatively short time span in which cobalt-chromium base alloys processed by means of CAD/CAM technologies have been employed on a large scale in dentistry, the assessment of their corrosion behavior by closely simulating the conditions within the oral cavity necessitate further investigations.

2. Experimental

Two cylindrical samples with the base diameter of 10 mm and 2 mm height were employed in two distinct manufacturing processes, namely: the melting-casting technique using a commercial Co-Cr base material and the CAD/CAM milling technology using prefabricated Co-Cr dental alloy blocks. The chemical composition of the investigated probes, as given by the manufacturer, is detailed in Table 2. The samples employed in the CAS technique were firstly made of wax, invested and casted using a vacuum pressure casting machine. The samples were divested after cooling down, air-blasted with alumina particles and mechanically finished and polished using specific instruments. The samples manufactured by CAD milling were obtained using a 5 axis milling machine from a prefabricated block of type 4 Co-Cr dental alloy. Oxide-firing (at 950 – 980°C) was performed, as required for porcelain veneering for all samples, the metal surface was blasted with fresh aluminum oxide (75 µm).

All samples were finally finished using silicon carbide sheets and 1µm grit diamond paste respectively, degreased and sonicated in distilled water, rinsed and dried prior to undergoing electrochemical investigations. Electrochemical investigations have been undertaken using a BioLogic SP150 potentiostat/ galvanostat equipped with an EIS module 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 within frequencies ranging from 100 kHz to 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]

3. Results and Discussion

Dental restorations are being constantly exposed to the ever-changing conditions within the oral cavity and, since the content of sodium chloride in the human saliva is very close to that of seawater [15], corrosion of the base metal alloys becomes a key factor. In order to investigate the phenomena taking place at the metal - electrolyte interface, we've conducted several comparative electrochemical

measurements of the two types of samples in saline solutions at different temperatures, closely resembling the conditions in the oral cavity.

The corrosion behavior of the cast sample immersed in 3.5% aqueous saline solution was investigated by recording the Tafel polarization curves at four different temperatures (Figure 1). The manufacturing technique seems to exert a notable influence on the voltammetric response of the studied samples. While the corrosion potential of the casted sample (CAS) shifts towards more positive values with increasing temperature (Figure 1a), the sample obtained by CAD milling (MIL) shows only a slight deviation of the corrosion potential with respect to the increase of the solution temperature.

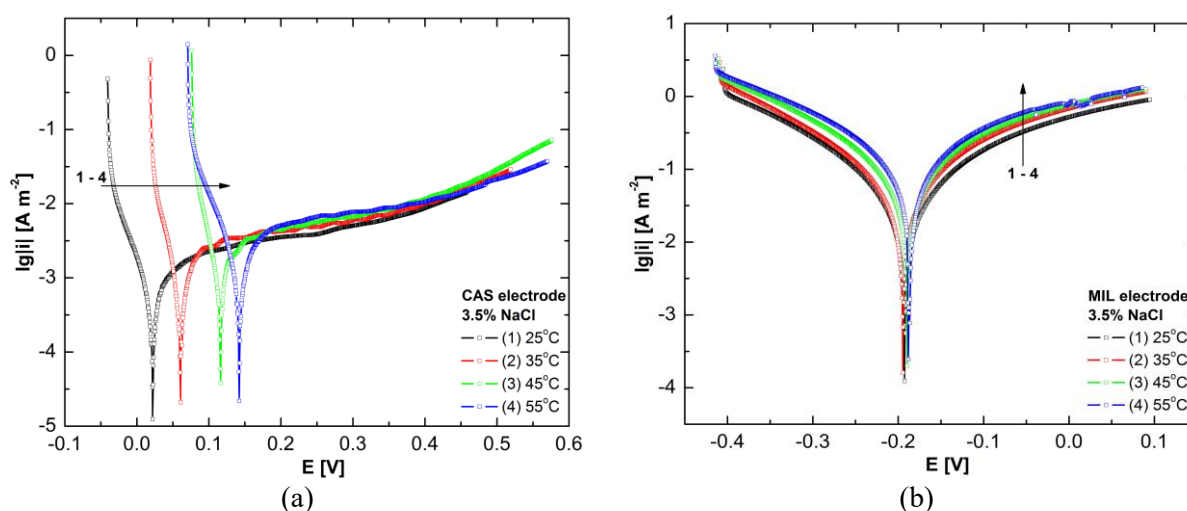


Figure 1. Tafel polarization curves recorded for the cast sample (a) and for the CAD milled sample (b) in 3.5% NaCl solution, at different temperatures and a scan rate of $1 \text{ mV} \cdot \text{s}^{-1}$

The classically manufactured CAS sample exhibits a sharp current density increase at potentials below 50 mV (at 25°C), most probably due to the reduction of physically dissolved oxygen or the reduction of H^+ ions. The first process being more likely to occur noting that deaeration of the electrolyte solution has not been undertaken prior to the voltammetric measurements. Scanning towards more positive potentials reveals the active-passive region, characterized by a swift decrease of the current density, followed by a relatively large passivation region extending from about 100 mV to about 250 mV (at 25 °C) where the current density remains almost constant. Passivity seems to partially break down at potentials higher than 250 mV (at 25°C), probably due to the presence of Cl^- anions [16] suggesting a transpassive region with a slight current increase at potentials up to 550 mV, where the passivating film is most probably dissolved and water is oxidized. This behavior, is in accordance with other literature data [17]. Temperature increase of the electrolyte solution leads to a shift of the corrosion potential (E_{corr}) towards more positive regions, altogether with the passivation plateau and the transpassive zone.

The data for the CAD-manufactured (MIL) sample differ significantly in terms of electrochemical corrosion response (Figure 1 b). In this case, the corrosion potential remains relatively stable at about -190 mV over the whole temperature array, suggesting a higher susceptibility towards electrochemical corrosion compared to the CAS sample. The potentiodynamic analysis reveals a highly symmetrical behaviour of the cathodic region compared to that of the anodic field, both sides showing transpassive regions with a sharp current increase at about -400 mV probably due to oxygen reduction, with no passivating plateau.

Tafel parameters, corrosion rate (v_{corr}), as well as other significant electrochemical data like corrosion current density (i_{corr}), corrosion potential, polarization resistance (R_p), recorded for each of

the two samples at various electrolyte temperatures are detailed in Table 1. The data reveals that, the more negative corrosion potential in the case of the CAD milled (MIL) sample is in accordance to its corrosion rate which is significantly higher compared to the casted (CAS) sample, probably due to the lack of a compact and nonconductive passivating coating.

Table 1. Polarization parameters for the corrosion behaviour of the investigated samples in 3.5% NaCl electrolyte at various temperatures

Sample	T [°C]	i_{corr} [$\mu\text{A cm}^{-2}$]	E_{corr} [mV]	$-b_c$ [mV dec $^{-1}$]	b_a [mV dec $^{-1}$]	R_p [k Ω]	$v_{\text{corr}} \cdot 10^3$ [mm year $^{-1}$]
MIL	25	5.85	-197	195	160	10.7	73.2
	35	7.77	-194	203	163	7.91	106
	45	12.57	-190	239	187	5.92	171
	55	17.83	-186	265	208	4.73	243
CAS	25	0.054	22.1	304	29.7	163	1.42
	35	0.180	71.1	333	25.5	128	2.45
	45	0.244	103	362	21.9	101	3.32
	55	0.290	117	401	27.2	86.7	4.06

In order to elucidate the corrosion behaviour of the investigated probes, we recorded the corresponding cyclic voltammograms in 3.5% saline solution at four different temperatures at a scan speed of 100 mV s $^{-1}$. The recorded voltammetric data covered a wide potential domain, reaching from a negative value of about -1.25 V, towards the Hydrogen evolution reaction, to a positive polarization of 1.25 V at which the metal ion release from the base alloy is likely to take place. A relative outcome of the obtained cyclic voltammograms for the two studied samples is shown in Figure 2b.

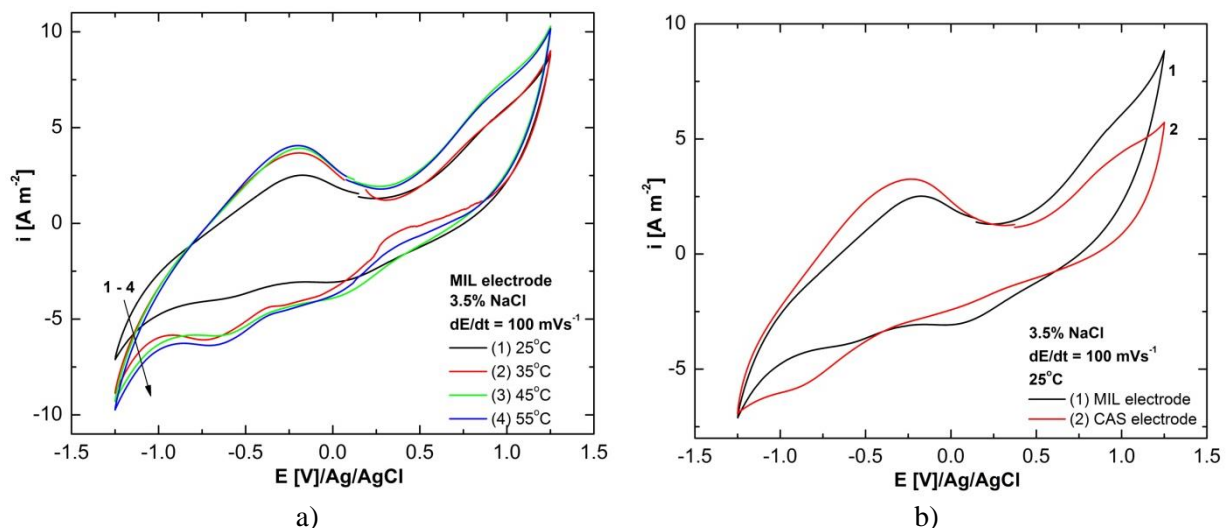


Figure 2. Cyclic voltammograms recorded in 3.5% NaCl electrolyte at a scan rate of 100 mV s $^{-1}$ for the MIL sample at different temperatures (a) and superimposed for MIL and CAS samples at 25°C (b)

Varying the potential from the open circuit potential towards more positive values on the MIL sample, reveals a steady increase of the current density recorded for all measured temperatures, however, a gap is observed between the recordings for 25-35°C and 45-55°C respectively. A weakly defined peak at about 0.8 V is revealed before the current increases due to the oxygen evolution reaction. The reverse scan shows a weakly defined signal at about -0.1 V and a sharper peak at -0.6 V. The latter maximum does not occur at a temperature of 25°C and seems to be linked to a relatively

broad signal occurring at approximately -0.25 V within a quasireversible process. The cathodic scan is limited negatively by the hydrogen evolution reaction at potentials around -1.25 V.

The comparative view of the voltammograms recorded for the two samples at the same temperature reveals a significant difference in their electrochemical behaviour namely the CAS sample exhibits a wider passivating region thus being less susceptible towards corrosion, in accordance to the data obtained from the Tafel analysis, while the MIL sample does not reveal any passivating zone at all.

Both samples have been subjected to chronoamperometric studies in 3.5% saline solution at the whole array of temperatures, as shown in Figure 3, with the aim of additionally clearing up the corrosion conduct of the investigated probes.

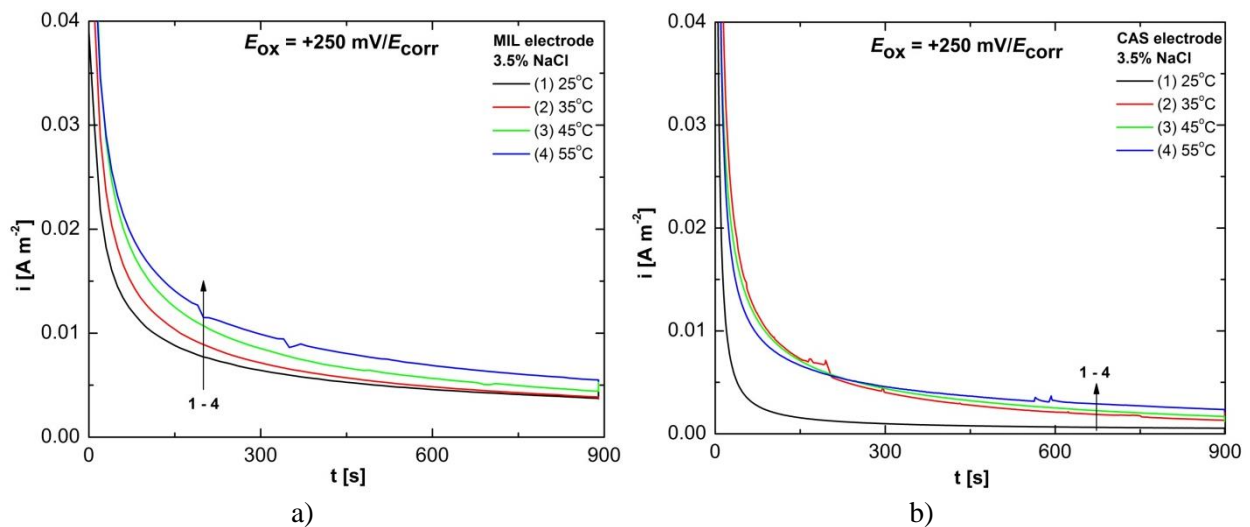


Figure 3. *i-t* plots recorded at +250 mV vs. E_{corr} , for the anodic oxidation of MIL (a) and CAS (b) samples in 3.5% NaCl solution at various temperatures for 15 min.

Chronoamperograms for both samples at various temperatures have been raised at an applied potential of +250 mV vs. E_{corr} by recording the current flow over a period of 15 minutes. Both samples exhibit rapid decrease of the corresponding current densities but there are some noteworthy differences. The MIL sample shows a slower but steady decrease of the current at all temperatures while the CAS sample exhibits a nearly exponential current decay followed by a plateau at 25°C while higher temperatures generate a much slower decrease of the current density, probably due to a more stable and adhering oxide coating formed at the metal surface as well as an increase of the interfacial resistance, as suggested by the literature [18]. The samples reveal different slopes of the constant current region, suggesting distinct mechanisms and rates of the corrosion process. Significantly higher currents have been recorded for the probes obtained by CAD milling compared to those manufactured by classical casting procedures.

Table 2. Composition of the investigated samples (expressed as percentage by weight)

Sample	Co	Cr	Mo	Mn	W	Si	Fe	C
CAS	61.5	26	6	<1	5	<1	<1	0
MIL	61	28	0	0.25	8.5	1.65	<0.5	<0.1

In order to further investigate the mechanism of the corrosion processes taking place at the surface of the studied samples, electrochemical impedance spectra (EIS) have been recorded. Impedance studies have been conducted at the corresponding corrosion potentials (E_{corr}) in aqueous 3.5% NaCl solution within a temperature range between 25 and 55°C. The obtained results are depicted as

Nyquist and Bode plots for the samples obtained by CAD milling (Fig.4) and casting (Fig.5) respectively.

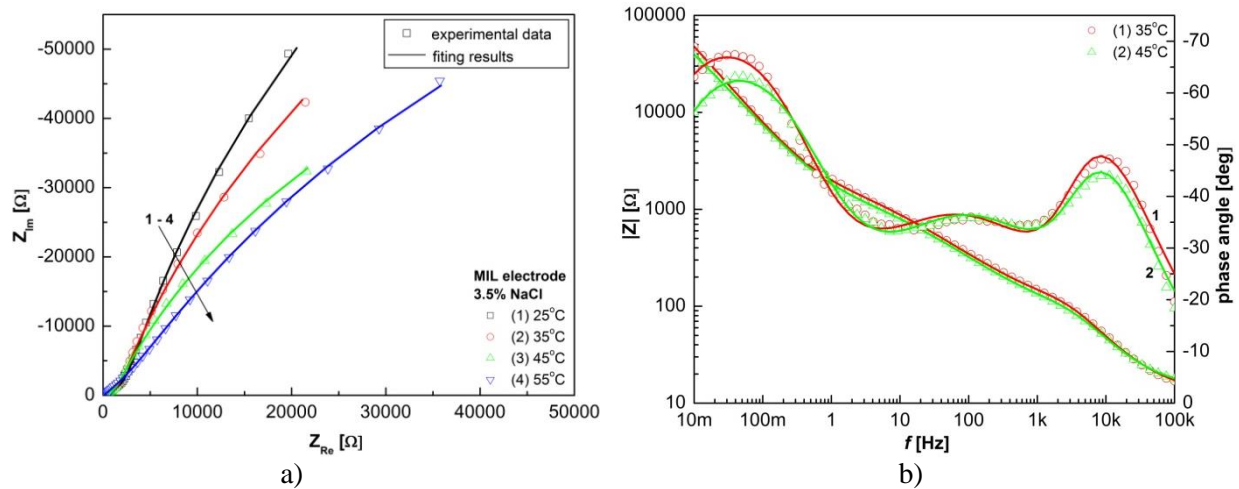


Figure 4. Nyquist (a) and Bode plots (b) recorded at the corresponding corrosion potentials on MIL samples in 3.5% NaCl solution at various temperatures

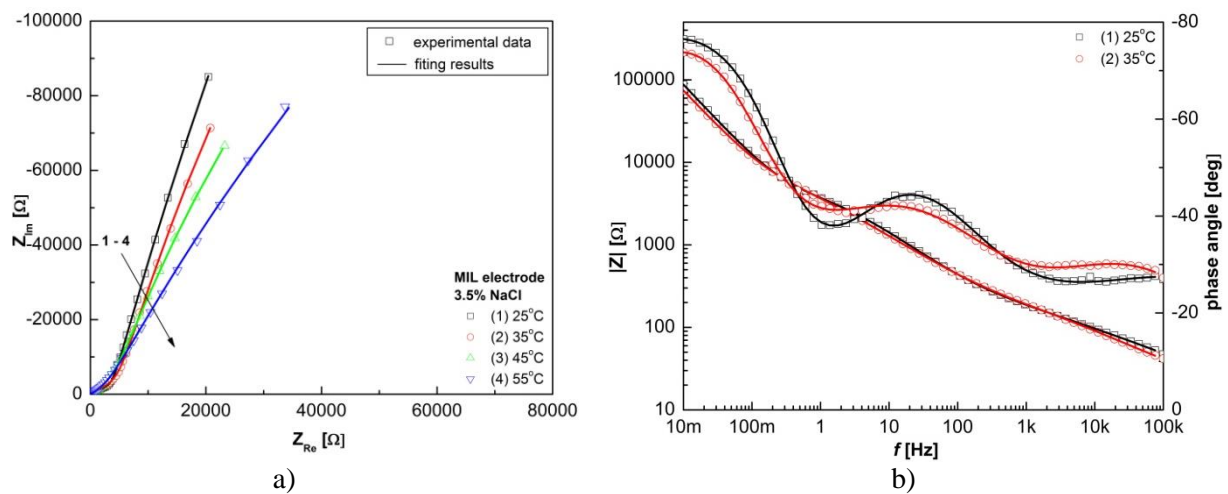


Figure 5. Nyquist (a) and Bode plots (b) recorded at the corresponding corrosion potentials on CAS samples in 3.5% NaCl solution at various temperatures

The obtained results on the investigated dental alloys lead us to propose an equivalent electrical circuit (EEC) of the type $R_s(CPE_{pore}R_{pore})(CPE_{film}R_{film})(CPE_{dl}R_{dl})$ based on a three layer structure to fit the EIS data. The layers are most probably composed of an inner compact film and an outer relatively porous passive film, as shown in Figure 6, in order.

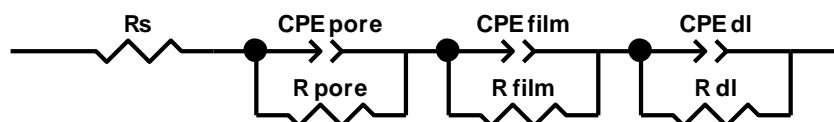


Figure 6. Equivalent electrical circuit model used for fitting the recorded EIS spectra

The EEC consists of the solution resistance R_s in series with three parallel connections consisting of the charge transfer resistance R and a constant phase element (CPE), each of the connections being specific to the layers mentioned above, while R_s represents the uncompensated solution resistance. In order to closely simulate a real electrochemical system, the ideal capacitor (C) is usually replaced by a constant phase element (CPE) because it represents the processes that take place at the electrode/electrolyte interface more accurately. The impedance of the CPE element is given by Equation (1):

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

where T is a parameter proportional with the double layer capacity, n is an exponent ranged between 0 and 1 which describes CPE angle.

The terms CPE_{pore} and R_{pore} represent the constant phase element for the capacitive behavior and the resistance of the outer, relatively porous, passive film, the third, most outer layer formed on the electrode surface. CPE_{film} and R_{film} stand for the constant phase element and the resistance characteristic for the impedance response of the inner compact film. CPE_{dl} and R_{dl} are used to describe the charge transfer process occurring at the interface of the investigated dental alloys. The fitting results are depicted as continuous lines in Figures 5 and 6 whereas the hereby obtained values for the circuit elements corresponding to the corrosion process of the CAD milled (MIL) and the conventionally casted (CAS) samples determined in 3.5% NaCl electrolyte are given in Table 3. The values for the double layer capacity have also been computed.

Table 3 Calculated values of the EEC elements for the corrosion process of the studied MIL and CAS samples in 3.5% NaCl electrolyte

Samples	T [°C]	R_s [Ω cm ⁻²]	porous passive film			compact film		
			$T \cdot 10^5$ [F cm ⁻² s ⁿ⁻¹]	n	R [Ω cm ⁻²]	$T \cdot 10^5$ [F cm ⁻² s ⁿ⁻¹]	n	R [Ω cm ⁻²]
MIL	25	14.6	10.6	0.58	2406	0.17	0.87	118
	35	11.2	9.26	0.57	1833	0.20	0.88	91
	45	12.8	8.99	0.56	1511	0.35	0.90	71
	55	14.8	8.72	0.55	1234	0.33	0.91	47
CAS	25	4.74	6.2	0.52	225	4.52	0.47	4048
	35	4.56	5.0	0.50	190	7.83	0.50	3704
	45	7.51	4.1	0.47	167	10.4	0.52	3496
	55	8.33	3.4	0.45	139	12.2	0.56	3011

Samples	T [°C]	charge transfer process			$C_{dl} \cdot 10^4$ [F cm ⁻²]	$Chi^2 \cdot 10^4$
		$T \cdot 10^5$ [F cm ⁻² s ⁿ⁻¹]	n	$R_{dl} \cdot 10^5$ [Ω cm ²]		
MIL	25	20.2	0.87	3.51	3.82	5.56
	35	15.1	0.83	2.68	3.22	8.47
	45	10.6	0.79	1.60	2.25	4.27
	55	6.48	0.73	1.07	1.33	1.85
CAS	25	16.7	0.89	32.0	4.15	0.56
	35	14.2	0.86	26.6	3.73	0.84
	45	12.5	0.83	17.1	3.61	0.91
	55	10.7	0.80	10.9	3.52	0.38

The similar shape of the impedance spectra shown in Fig. 3 and 4 as well as the use of the same equivalent electrical circuit (EEC) shown in Figure 5 for the fitting of the experimental impedance spectroscopy data obtained for the corrosion study of the investigated Co-Cr alloys obtained through CAD milling and by conventional casting in 3.5% aqueous NaCl, suggests highly similar mechanisms governing the processes taking place at the dental alloy/electrolyte interface for the two samples. Although the corrosion most probably implies the formation of two layers of metal oxides on the surface of the alloy, one being porous whereas the second being a more compact passivating layer, there are notable differences concerning the corrosion rate of the two probes. Considering the values of the charge transfer resistance for each of the two layers, we can assume that the forming of the porous oxide layer is favoured on the MIL sample whereas on the CAS probe the compact passivating oxide layer seems to be predominant, conferring a higher corrosion resistance of the base alloy. The charge transfer resistance R_{dl} is proportional to the corrosion rate, *i.e.* the smaller the resistance, the faster the corrosion process will occur. Taking into account that the values of R_{dl} corresponding to the CAS sample are up to an order of magnitude greater than those obtained for the MIL probe is an indication for a significantly higher corrosion resistance of the first within the investigated medium, compared to the latter. As is to be expected, the rate of corrosion in saline solution rises along with the temperature increase within the extent between 25-55 °C for the samples obtained through CAD milling (MIL) as well as for the casted ones (CAS). With the aim of undertaking an in-depth analysis of the studied corrosion phenomena, we determined the capacity of the double layer (C_{dl}) for each sample at temperature values within the investigated array. The relatively high values for C_{dl} exhibited by the CAS sample stand for a greater resistance towards corrosion.

4. Conclusion

The presented electrochemical studies conducted in 3.5% NaCl solution reveal a greater resistance towards corrosion associated to the Co-Cr dental alloys obtained through casting compared to the ones manufactured by CAD milling, whereas the corrosion rate varied ascending, proportional to temperature, as expected.

The investigated dental alloys reflect notable differences regarding the electrochemical behaviour towards corrosion based on two completely different manufacturing technologies. The Tafel polarization curves as well as the impedance analyses acknowledge a relatively higher corrosion rate as well more negative corrosion potentials exhibited by the CAD processed sample. The corrosion potential of the casted sample varies strongly with temperature, whereas the CAD milled probe shows no such behaviour. More thorough investigations are necessary in order to determine the corrosion mechanisms of the two samples. The corrosion behaviour of the studied samples in the above mentioned medium resembles the one determined in artificial saliva [19].

The electrochemical impedance data revealed that two layers are formed on the surface of the investigated probes in aqueous 3.5% NaCl electrolyte, one being more porous and the second being compact with a passivating effect. The growth of the second protecting layer being favoured on the surface of the CAS sample results in a greater protection thus a higher resistance towards corrosion of the probe crafted by conventional casting.

5. References

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