TRACING THE CORROSION PROCESSES OF DIFFERENT METAL-CERAMIC DENTAL CROWNS BY EIS AND SEM INVESTIGATION

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The paper aims on the investigations of corrosion processes of three different porcelain fused to metal dental crowns with CoCrMo frameworks. The three crowns, with different exposed metal surfaces, were investigated using electrochemical impedance spectroscopy (EIS), through 168 hours of experiment. The data were analyzed and the influence of corrosion processes was shown after the crowns were visualized as equivalent electrical circuits. Scanning electron microscopy (SEM) coupled with EDX was used to analyze the crowns surfaces.

Keywords: electrochemical impedance spectroscopy, metal-ceramic crown, equivalent circuits, scanning electron microscopy

1. Introduction

Metal-ceramic crowns are widely used in restorative dentistry in order to rehabilitate the functionality and aesthetics of teeth which have been lost. Dental alloys are used in dentistry for fixed prosthodontics, implants and orthodontics [1, 2]. In porcelain fused to metal restorations the dental alloys are casted as metal substructure on which the ceramic is chemically bounded after firing. The metal substructure, especially the modified ones [3, 4], offers strength and stability due to the passive layers formed on its surface[5], while ceramics give an aesthetic appearance of the prosthodontics [6].

Metal ceramic restorations have been used in dentistry for more than 50 years. The ceramics used in this technological processes are usually based on potassium aluminium silicate [7]. The metal substructure is obtained after dental alloys are casted into molds. High and low content gold alloys, titanium, silver-

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palladium, nickel-chromium and cobalt-chromium alloys are used to obtain the metal framework. Nickel chromium and cobalt chromium are widely used as casting alloys as they have a lower cost, better modulus and creep resistance during firing processes. Unfortunately, these alloys can suffer corrosion and release ions in the oral environment [8].

Even if the use of dental alloys should be safe and biocompatibility problems should not appear, oral lesions related to the toxic, irritant and allergic nature can occur [9].

Corrosion processes which involve ion release from the dental alloys in the oral cavity can lead to failure of the metal ceramic restorations, with decrease in mechanical resistance, leading to discoloration of natural teeth or soft tissue metallic pigmentation [10]. Taking into account that corrosion process is a chemical or electrochemical reaction with gradual destruction of a metal or metals in their environment, the oral environment enhances the biodegradation of the metal framework, the biocompatibility can be affected due to corrosion processes which occur. There are many factors such as mechanical loads[11], pH and temperature variations and wear which can lead to biocompatibility issues [12, 13].

Electrochemical impedance spectroscopy (EIS) is a powerful, non-destructive experimental technique in which a small alternating amplitude current signal is applied to conductive materials such as alloys, metals, polymers, ceramics[14]. In the dentistry field, EIS technique can be used to analyze the behaviour of the hard dental tissues such as enamel, dentine, cavity filling materials such as glass - ionomer cement, light-cured dental resin[15] or in the field of dental alloys and dental ceramics [16].

2. Materials and methods

Three different metal ceramic crowns (Fig. 1) were obtained in a dental laboratory in order to analyze the corrosion processes which occur when these restorations are placed in a simulated body fluid (SBF) aqueous solution which simulates the oral environment. The first crown (Crown 1) was a metal ceramic crown on which the ceramic entirely covered the metal substructure. The second crown (Crown 2) had a metal collar on its lingual face in order to reduce the undesired plaque accumulation, while the third crown (Crown 3) had a ceramic veneer on its buccal face for aesthetic considerations, and a wider exposed metal surface.

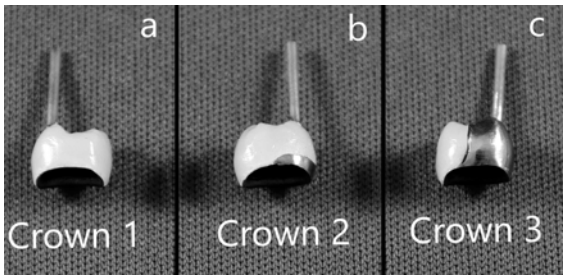

Fig. 1. The porcelain fused to metal crowns. Crown 1 has the metal substructure covered entirely with ceramics, Crown 2 has a metal collar on its lingual face , while Crown 3 has aceramic veneer on its buccal face and a wider exposed metal surface

All three crowns were cemented on zirconia abutments. The zirconia abutments were obtained after three identical cylinders have been milled from a standard pre-sintered zirconia CAD/CAM milling disc blank, (Degos Dental). After the abutments were prepared, their surface was mechanically treated by air-blasting with 100 μm alumina particles to enhance later adherence of the dental cement. Later on, the porcelain-fused-to-metal crowns were fabricated using standard dental laboratory techniques. The metal substructure was obtained by casting the CoCrMo ingots into copings, using a centrifugal casting machine (Ugin Dentaire, Ducatron Serie 5). The dental casting alloy was a CoCrMo alloy (Vera DPI^{TM} from AalbaDent) and had the following composition: Co 63.5%, Cr 27.0%, Mo 5.5%, Fe 2.0%, Ni, Si, Mn. In order for the dental porcelain to properly bond to the metal surface, the copings were conditioned. The conditioning of the metal pieces took place in several steps, starting with the removal of surface imperfections by using different shaped extra-hard tungsten-carbide metal burs (Jota, Komet, Bredent). Then, the surface was air blasted with 125 μm alumina particles at a 45° angle with the axial surface, followed by a 6 bar pressure steam cleaning performed with a Silfradent EV1 Steamline vaporizer to remove any residue. A thin coat of ceramic bonding agent was applied on the surface of the copings and then they were set in a dental ceramic furnace at 960°C for 1 minute under vacuum.

The ceramic system used for the veneering of the metallic copings was Carmen CCS (Compact Ceramic System) which is a feldspar porcelain supplied by Dentaurum. For sintering of the ceramic, a Ney Centurion Q100 dental furnace was used. The porcelain was applied by using the brush layering technique following the producer's firing guide.

2.2 EIS and SEM/EDX measurements

In order to analyze the corrosion processes, the crowns were introduced as working electrodes in an electrochemical cell. A 10 mV sine waveform

perturbation was applied to the electrode potential, while the scanning modulus of impedance and the phase shift in the frequency ranged from 100 kHz - 0.1Hz. The measurements were carried out using a potentiostat / galvanostat Autolab from Metrohm Company. The electrochemical cell contained three electrodes: a working electrode (Crowns 1 - 3), a reference electrode (Ag/AgCl/3M KCl), a platinum counter-electrode and a simulated body fluid (SBF) electrolyte solution, prepared according to literature [17](Table 1) using bidistilled water. The EIS results were analyzed using Nova 1.9 Metrohm AutoLab software. SEM images were obtained after the 168 hours of samples immersion using a scanning electron microscope HITACHI, S-2600N Model, provided with EDX device.

Table 1

SBF composition

NaCl	7.996 g/L
$NaHCO_3$	0.350 g/L
KCl	0.224 g/L
$K_2HPO_4 \cdot 3H_2O$	0.228g/L
$MgCl_2 \cdot 6H_2O$	0.305 g/L
$CaCl_2$	0.278 g/L
Na_2SO_4	0.071 g/L
$(CH_2OH_3)CNH_2$(tris)	0.057 g/L
1M HCl solution was used for pH adjustment at 7,25	

3. Results and discussions

The eight EIS measurement for each sample were carried out at initial time of immersion (t = 0 hours) and over 168 hours of experiment.

The results of the EIS investigations are represented graphically using a complex plane Nyquist plot (imaginary part of the impedance, Z'' *vs.* real part of the impedance, Z') both for t = 0 hours and t = 168 hours.

Figures 2 a, 3 a, and 4 a show Nyquist diagrams plotted with measured data and fitted using equivalent circuits for Crown 1, Crown 2 and Crown 3, respectively.

For all samples, tested at t = 0, a Randles equivalent circuit (Figs. 2 c, 3 c, and 4 c) was proposed, consisted of an active electrolyte resistance R_1 in series with the parallel combination of the charge transfer resistance (R_1) and double-layer pseudo-capacitance expressed as a constant phase element (CPE_1) which takes into account a non-ideal capacitance resistance. The n exponent factor which represents the constant phase element power is a parameter which describes a perfect resistive behavior at an n factor when has value of 0 and a perfect capacitor when has the value of 1. The term Y0 of CPE shows the capacitance of the electrochemical double layer.

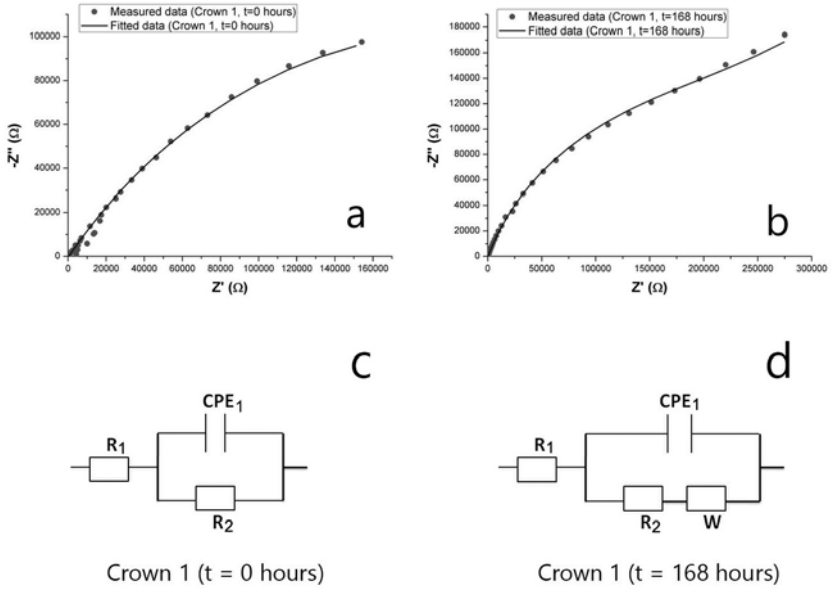

Fig. 2. Nyquist diagrams with measured data and fitted data for Crown 1, at t = 0 (a) and at t = 168 hours (b); proposed equivalent electrical circuits used for Crown 1 sample data fitting at t = 0 (c) and at t = 168 hours (d).

For Crowns 1 and 2 tested at t = 168 hours the proposed equivalent circuit was supplemented with a Warburg impedance (W) which has been assigned to diffusion processes through the ceramic layer. Thus, the Warburg diffusion element (Warburg impedance), with a value of the n exponent factor of 0.5 reveals a diffusive element in the proposed circuits.

For Crown 1 sample, by comparing the real resistive component (Z') of the impedance corresponding to the last experimental point at the lowest frequency (0.1 Hz) from Nyquist plots at t = 0 and t = 168 hours (Fig 2a and 2b) it can be seen an increase of the resistance, at low frequency, from 160 kΩ to 300 kΩ which may be associated with passivation processes on the metal surfaces. However, the charge transfer resistance, R_2, obtained from the data fitting (Table 2) shows a decrease from 424 kΩ, at t = 0, to 294 kΩ at t = 168 hours, suggesting rather changes in the diffusion process through the ceramic layer.

For Crown 2 (Fig. 3) tested at t = 168 hours the proposed equivalent circuit was supplemented with a Warburg impedance (W) which has been assigned to the diffusion processes through the ceramic layer and with a parallel R_3-CPE_2 circuit corresponding to metallic surface non-covered with ceramics, Fig. 3d. The components of this second circuit illustrate an ohmic resistance, R3,

due to a passive layer consisted in corrosion products and a constant phase element, CPE2, assigned to pseudo-capacitance of this layer.

The increase of the real resistive component of the impedance from Nyquist plots (Z'), for experimental points at low frequency, from 100 kΩ to 200 kΩ at t = 0 hours and t = 168 hours (Fig. 3a and 3b) suggests complex processes that take place through the ceramic film and/or at the metal/ ceramic interface.

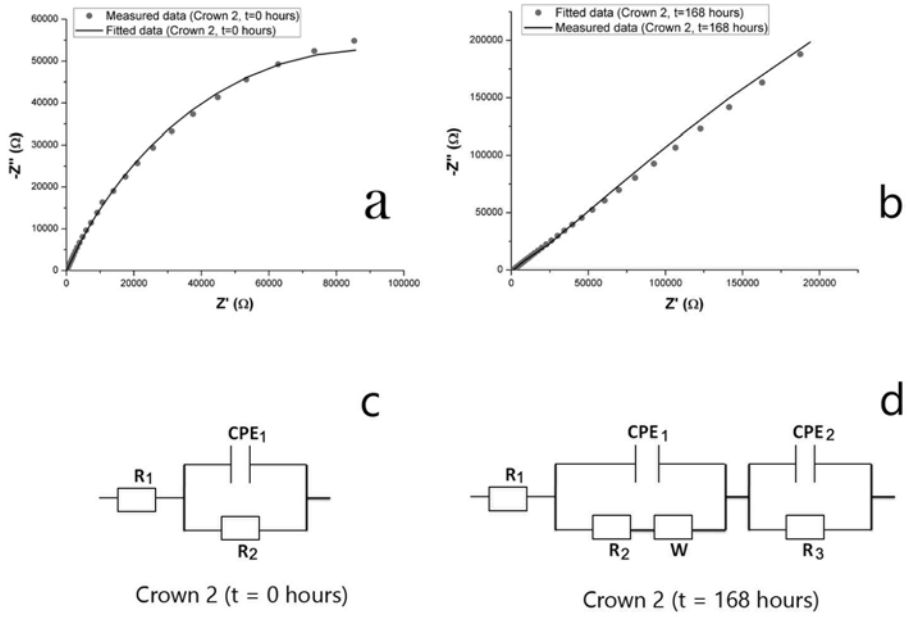

Fig. 3. Nyquist diagrams with measured data and fitted data for Crown 2, at t = 0 (a) and at t = 168 hours (b); proposed equivalent electrical circuits used for Crown 2 sample data fitting at t = 0 (c) and at t = 168 hours (d).

For Crown 3 (Fig. 4), the sample where the most of the metal surface is non-protected, the proposed second equivalent circuit has not been added, but a constant phase element for low frequency, CPE_2, was added.

The fitted value of charge transfer resistance R_2, is 16.7 kΩ which is very closed to 18.6 kΩ, value of R_3 from electrical circuit proposed for Crown 2.

An other interesting observation is that the real resistive component of the impedance from Nyquist plots (Z'), at low frequency, (Fig. 4a, 4b) decreases in this case, from 60 kΩ to 10 kΩ which is a supplementary evidence that the increasing of the resistive impedance component observed for Crown 1 and Crown 2 is rather due to complex processes through the ceramic film and less to the passivation processes on metallic surface.

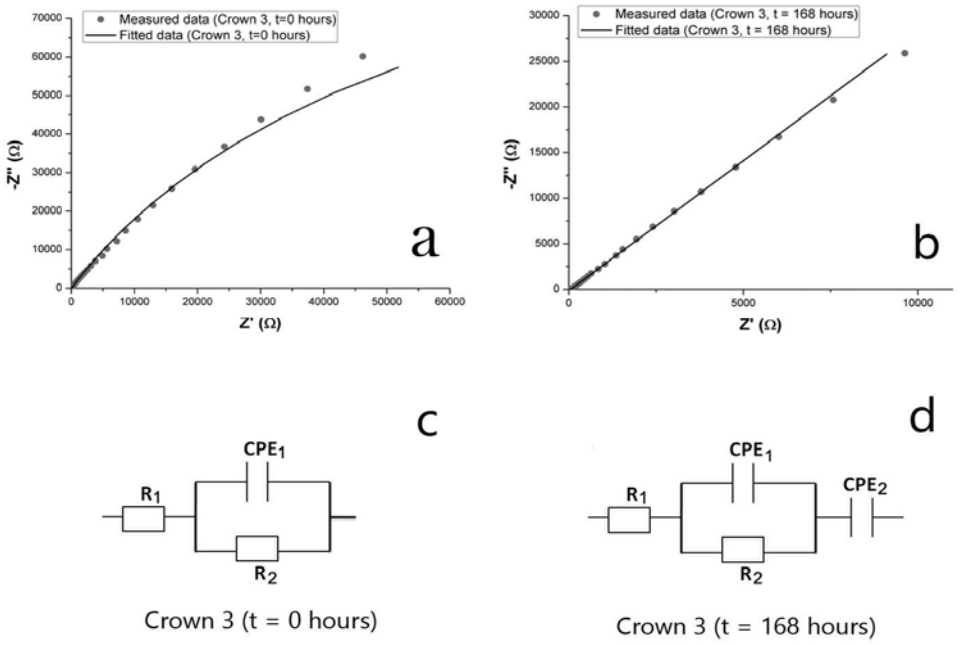

Fig. 4. Nyquist diagrams with measured data and fitted data for Crown 3, at t = 0 (a) and at t = 168 hours (b); proposed equivalent electrical circuits used for Crown 3 sample data fitting at t = 0 (c) and at t = 168 hours (d).

Table 2

Values of the electrical elements in electrical ciruit for Crowns 1 – 3 at t = 0 and t = 168 hours

	R1 (Ω)	R2 (kΩ)	CPE 1		W		R3 (kΩ)	CPE 2	
			n	Y0 (μMho)	n	Y0 (μMho)		n	Y0 (μMho)
Crown 1 (t = 0)	330	424	0.576	4.99	-	-	-	-	-
Crown 1 (t = 168 hours)	102	294	0.734	1.50	0.5	7.31	-	-	-
Crown 2 (t = 0)	60.6	179	0.677	8.17	-	-	-	-	-
Crown 2 (t = 168 hours)	100	69.1	0.763	0.969	0.5	100	18.6	0.153	114
Crown 3 (t = 0)	32	231	0.729	14.8	-	-	-	-	-
Crown 3 (t = 168 hours)	38	16.7	0.893	26.2	-	-	-	0.785	52.7

The elemental chemical analysis illustrated by EDX spectrum of Crown 1 (Fig. 5) revealed a content of Si, Al, Ca, K and Na which indicated a feldspathic porcelain, revealing a very good adhesion of the ceramic mass to the metal framework.

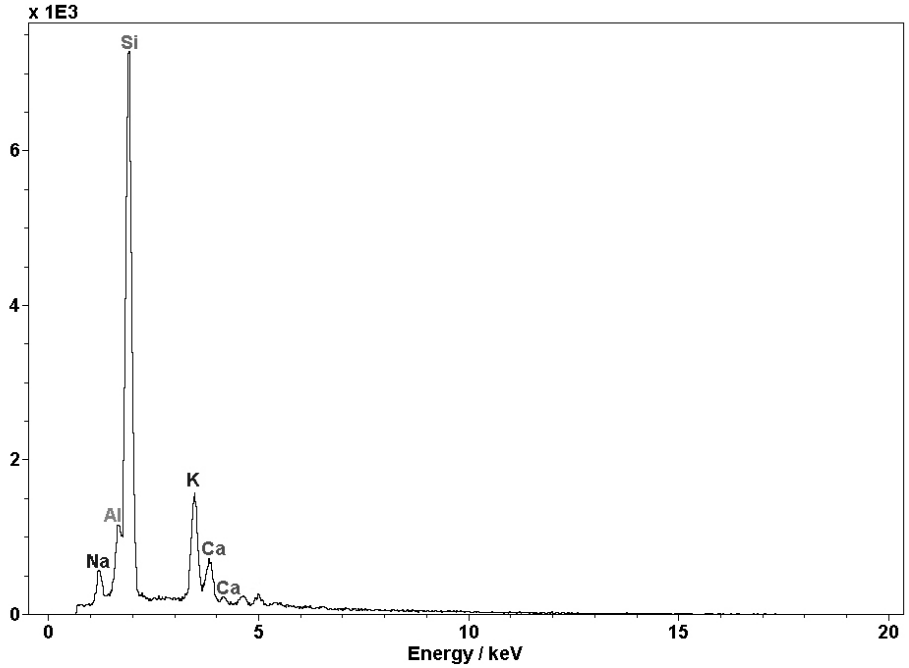

Fig. 5. EDX spectrum of Crown 1 sample which indicates a feldspathic porcelain.

The SEM images (Figs. 6) were obtained at the end of the 168 hours of immersion. In Fig. 6a it can be seen a good marginal adaptation of the porcelain fused to metal crown on the zirconia abutment after cementation with a glass ionomer cement. In Fig. 6b the porcelain had a good adhesion after burning to the CoCrMo substructure. In fig 6c and Fig. 6d it could be seen a relatively homogeneous structure of the ceramic mass characterized by a certain porosity.

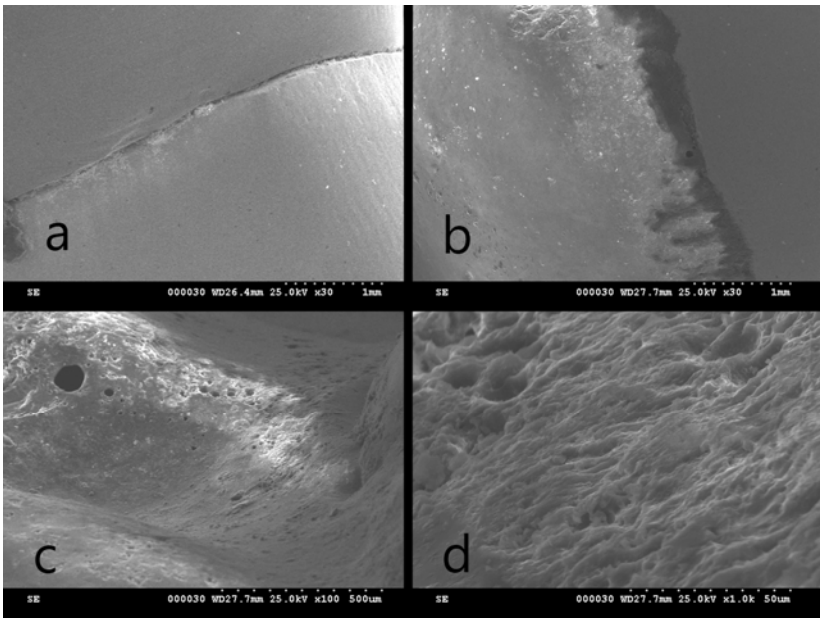

Fig. 6. Scanning electron microscopy images at different magnifications. Fig. 6a shows a good marginal adaptation of the metal-ceramic crown to the zirconia abutment. Fig. 6b shows a good adhesion of the ceramic mass to the metal copings. Fig. 6c-d reveals a homogenous mass of the ceramic mass.

6. Conclusions

Three different metal ceramic crowns obtained in a dental laboratory were analyzed in a simulated body fluid (SBF) solution in order to highlight the corrosion processes which occur when these restorations are placed in oral environment. EIS data analyzed in terms of the resistive component of the impedance and the electrical parameters of the equivalent circuit suggest complex processes that take place through the ceramic film and/or at the metal/ceramic interface. For Crown 1 and Crown 2 a Warburg impedance element was introduced in the equivalent circuit which has been assigned to diffusion processes through the ceramic layer. As expected, increasing coverage of metal with ceramic coating has led to an increase in the resistive component of impedance.

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