Modern Methods for Assessing the Corrosion Resistance of Dental Alloys Used in Dentistry

Ion Patrascu, Vlad Gabriel Vasilescu and
Stefan Milicescu

Additional information is available at the end of the chapter

1. Introduction

The corrosion process involves a sequence of reactions in which a metal or an alloy is attacked by an aggressive agent [4, 13]. Due to their particular electronic structure characterized by the presence of free electrons in the crystalline network, metals and alloys react chemically or electrochemically and thus may suffer corrosion processes [13, p.85]. The stabile chemical state of the metals is the combined one (oxides, hydroxides, other components) as they appear in the ore from which it was derived. In other words, the metals have a spontaneous tendency to return in a thermodynamically stable combined state through corrosion. Chemical Corrosion is the destruction of metallic materials after direct chemical action to occur without an environment changed by the electric charges. The products resulting from the interaction between the metal and environment remain on the metal surface in formats of thin films. The initial oxide layer/film has a thickness of 10 to 20A0, and then corrosive attack depends on its physical properties such as adhesion, compactness, porosity and the volume of this layer in relation to the volume of metal. The nature of the parent metal is determining both the thermodynamic stability and the properties of the oxide film formed on its surface. Some alloys have a corrosion resistance higher than that of the technical metals through their alloying elements (Al, Cr, Ni, Si) which allow the formation of protective oxide coatings. Electrochemical corrosion - represent destructive attack on metals or alloys exercised by the corrosive environment through electrochemical reactions, in which the metal releases electrons and its positive ions enter in solution. The formation of positive ions and electrons create an electrical potential (in volts) called electrode potential [28, 29].

Series electric potentials classify the chemical elements according to their tendency to gain (reduction) or lose (oxidation) electrons in electrolyte solutions, taking as reference the

electrical potential of the hydrogen which is conventionally assessed value of 0,000 volts. Elements that have negative values in this series of electric potentials are chemically unstable, highly reactive chemical that is very sensitive to aggressive environment. Instead, elements that have positive values of electrical potential are less reactive metals. Graphical representation of the balance between metal and its various oxidizing species is given in the diagram "potential - pH" in isothermal conditions or thermodynamic stability diagrams (Pourbaix diagram) [13]. They provide thermodynamic data about corrosion phenomena, indicating equilibrium conditions of all the reactions that can take place between the metal and the aggressive environment at a given temperature. Pourbaix Diagrams set only thermodynamic conditions in which chemical reactions can take place between the metal and the corrosive environment. Completing them with kinetic data gives real guidance on the extent of destruction of the metal in the environment.

2. Methods for assessing the corrosion resistance of metals and alloys

For the evaluation of corrosion processes one can use direct methods and indirect methods.

Direct methods consist in weighing or measuring thickness of samples, aggressive agent consumption or gas measurement resulting from corrosion processes. Indirect methods involve electrochemical measurements, electrical, acoustic, optical, etc.

In electrochemical methods the corroded metal is assessed by measuring the amount of current flowing in the process. The corrosion rate is obtained by reporting the amount to the area and time.

3. Corrosion of metals and alloys used as biomaterials

As discussed previously, corrosion is a type of damage in which the metal leaves its metallic state to form cations in solution or is converted into solid compounds (called corrosion products). The corrosion resistance of metallic materials used in oral implants is an important issue, expressing their biocompatibility. The state many metals are in an oxygenated environment or a hydrate one characterized by the lowest energy is that of the oxide. Corrosion occurs when the metal atoms are ionized and go into solution, or they are combining with oxygen or other substances to form a compound that is removed or dissolved. A variety of different chemical reactions take place when a metal is placed in an aqueous environment (Figure 1). The electrolyte containing ions in solution acts to close the electrical circuit. In the oral cavity, corrosion of metals and alloys is a galvanic corrosion which is produced by forming a electrochemical or galvanic cell in which the electrolyte is liquid cavity. Anions are negative ions, which migrate to the anode and the cations are positive ions that migrate to the cathode.
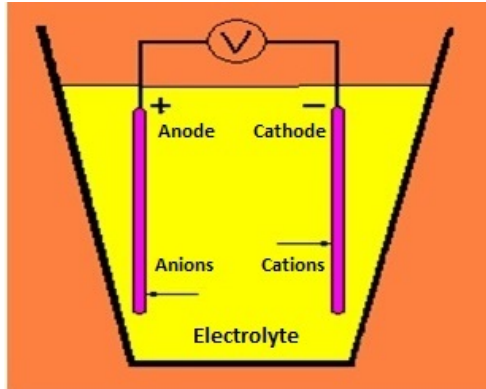
Figure 1. Electrochemic cell [29,p.53]

If two similar metals are present in the same environment, one that is the most negative in galvanic series will become the anode and bimetallic corrosion will occur (or galvanic).

Pourbaix diagram includes regions (zones) of corrosion, passivity and immunity, depending on the electrode potential and pH [13, 14]. Immunity is defined as the equilibrium between the metal and its ions less than 10^{-6} molar [29]. In the immune region the corrosion is energetically impossible. In the passivation domain, a stable solid constituent is an oxide, a hydroxide, a hydrate or a metal salt. Passivity is defined as a balance between a metal and its reaction products (oxide, hydroxide, etc.) at a concentration of less than 10-6 molar [29,p.55] g per liter atom (molar). This applies only if the reaction products (oxides) are adherents. In the field of biomaterials, passivity may be appropriate or not: the destruction of a passive layer can cause an increase in corrosion.
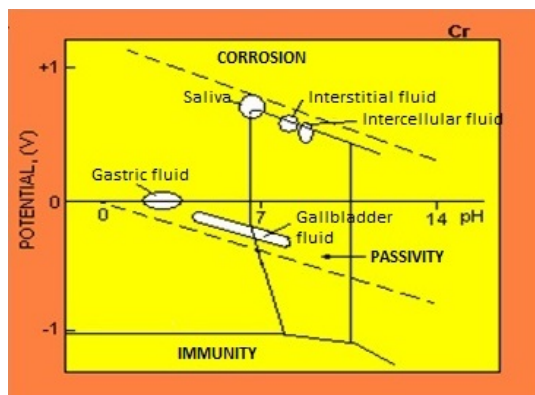

Figure 2. Pourbaix diagram for chromium (Cr) the regions associated with different body fluids (JHDumbleton and J.Black, An Introduction to Orthopaedic Materials, Charles C.Thomas, Springfield, 1975) [29]

As is known oral environment is a highly aggressive chemically, which is characterized by frequent changes in pH due to food and varied microbial flora present. On the other hand, the pH value may change more in the tissue that may be injured or infected. A liquid used in tissue has a pH of about 7.4, but in a wound can drop to values of 3.5, and the infection can reach values of 9.0 [29, p.57]
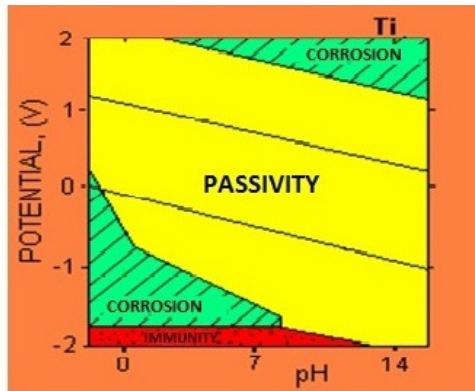

Figure 3. Pourbaix diagram for passive a metal (titanium) (after M.Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, NACE, Houston / CEBELCOR, Brussels, 1974) [29]

Experience shows that the main ways that may reduce the risk of galvanic corrosion in the oral cavity are:

1.   avoid using in the same oral cavity of metals with very different electrical potentials, the more so as they can come in direct contact (eg neighboring teeth);

2.   the use of homogeneous alloys, which do not occur with different electrical potentials phase

3.   avoid conditions that lead to plaque formation, given that the areas covered plate will present low pH, which can lead to corrosion.

4. Experimental conditions

Experimental Research on corrosion resistance of Co-Cr alloy biomaterial [25] were performed at Competence Center Tribocoroziune interfaces and electrochemical systems (CC-ITES) from the University "Dunarea de Jos" Galati."

4.1. Techniques and methods

The experiments were carried out at room temperature, 25°C, using the following techniques of investigation;

- The variation in time of the open circuit electrode potential (OCP)

- potentiodynamic polarization curves i (E),

- Cyclic voltammetry (CV),

- Records of electrochemical impedance spectra, more complex method for studying interface material / solution (EIS). These techniques have been applied to a potentiostat / galvanostat PGZ Voltalab 100 interface to the PC - soft VoltaMaster 4.

Electrochemical tests were performed on biomaterial, the chemical composition and mechanical properties in accordance with Table 1.

Chemical composition, %									
Specifications	EN 10204 -3.1B	Co	Cr	Mo	Mn	C	Fe	Si	Sonstige
	Max. [%]	63	29, 4	5, 95	0, 6	0, 29	0, 05	0, 7	0, 1
Properties									
Density g/cm3			Hardness HV10				Elasticity modulus, E Mpa		
8, 3			420				230.000		

Table 1. The chemical composition and mechanical properties of CoCr alloy [25]

We studied the corrosion behavior of Co-Cr alloy for biomedical applications, in aqueous solutions with different pH because it is known that all vital processes in the body is carried to the exact values of pH.

The solutions used in conducting the experiments are shown in Table 2. Were selected three types of media, so-called artificial saliva with different pH values: Hank (pH 7.4), artificial saliva Saliva Fusayama Meyer (pH 5.0) and Ringer's saliva (pH 6.6) seeking behaviors to study corrosion of Co-Cr alloy as metallic biomaterial.

The reason for the use and the choice of other media, such as citric acid is that it is a powerful oxidant and has a pH more acidic (pH 1.8), which can influence (formation, growth) of the oxide layer the surface of the sample.

4.2. Experimental results

The variation in time of the open circuit potential is a method of electrochemical oxidation which indicates the tendency of a material to a corrosive environment. After an immersion time it stabilizes around a stationary value.

To assess the kinetics of corrosion processes for the studied material were recorded under potentiodynamic polarization curves in the potential range from (-1500 mV) versus Ag / AgCl at (+1200 mV) versus Ag / AgCl, at a rate of sweeping the potential of 5 mV / s.

A -B zone is the cathode area, the B - C field the passive one and C – D the transpasivity field.

Potential values in different fields and solutions introduced are in Table 3. Also the table shows the passivation current density of the alloy in the tested solutions for the field of passivation.
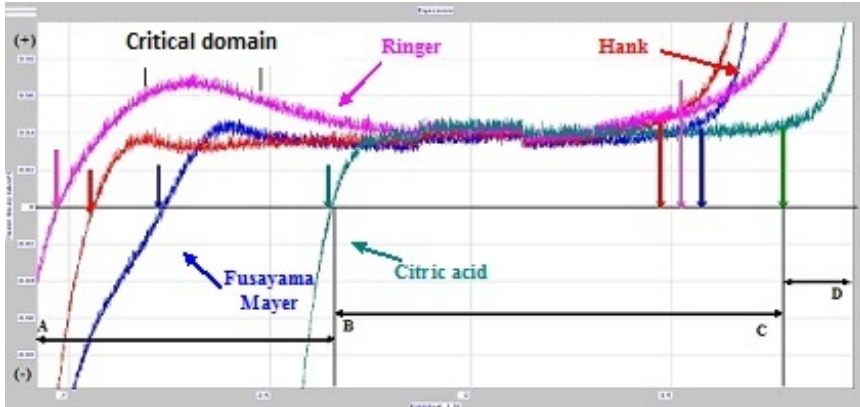

Figure 4. Identify of the passive areas on the potentiodynamic polarization curves for biomaterial Co-Cr immersed in the four environments [25, 26]

| Solution | Areas of potential, E [mV vs Ag/AgCl] | | | | |
| | Cathode | Critical | Passive | | Transpassive |
			E	$i_{passive}$ µA/cm²	
Fusayama Meyer (SFM)	< -764	-764 la -512	-512 la +569	36	> +569
Ringer	< -1030	-1030 la -390	-390 la +316	42	> +316
Hank	< -940	-940 la -750	-750 la +700	36	> +700
Citric acid	< -344	-344 la -135	-135 la +800	41	> +800

Table 2. The areas of potential and current density for passivation of the Co-Cr alloy [25, 26]

| Solution | Polarization resistance R_p [kohms cm²] | The corrosion potential E[mV vs Ag/AgCl] | The corrosion speed i_{cor} [mA/cm²] | |
			i_{cor} [mA/cm²]	µm/An
Fusayama Meyer (SFM)	0, 443	-902, 6	14, 16	153, 3
Ringer	3, 08	-1027	36, 80	398, 8
Hank	3, 0	-938	17, 27	187, 0
Citric acid	1, 69	-345	32, 99	357, 2

Table 3. The values of the polarization resistance and the corrosion current density of Co-Cr alloy in the Solutions tested [25, 26]

Areas with aspects of localized pitting corrosion phenomenon highlighted the qualitative analysis by electron microscopy (SEM - Scanning Electron Microscope, fig. 5) were further investigated specific techniques EDS equipment - Energy-dispersive X-ray spectroscopy quantitative analysis.
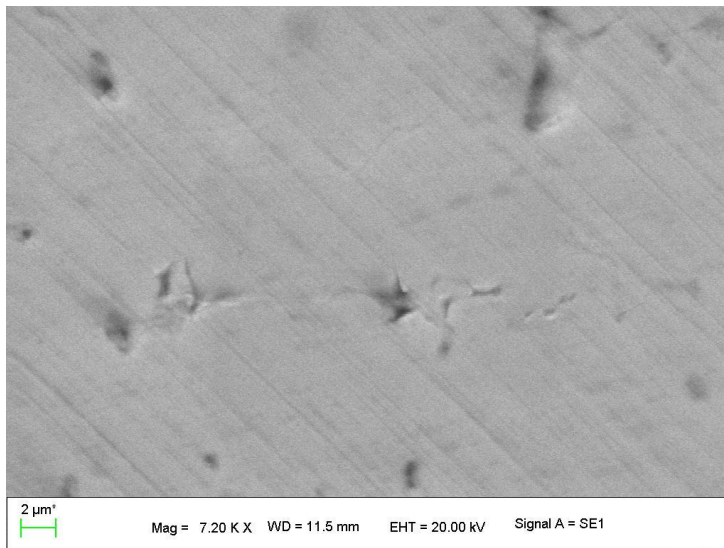

Figure 5. Micrographic aspects - details of the relief surfaces affected by corrosion (Magnification X 5000 using detectors BSE - Back-Scattered Electron Detector and SE-Secondary Electron Detector)[25]

5. Conclusions

- The used electrochemical methods (free potential, potentiodynamic curves, cyclic polarization, electrochemical impedance spectroscopy) are relevant methods for studying the materials/specific operating environment interactions.

- Results regarding the variation in time of the potential in open circuit as well as the results from the polarization curves under potentiodynamic regime show different levels of stabilization of the potential, but also different current densities depending on the pH.

- Polarization curves in potentiodynamic regime indicate the domain in which the passive oxide layer is destroyed through hydrogen release (area of instability), passivity domain of the formed oxide layer and the domain in which the dissolution of the metal occurs through the passive film and a deterioration of it.

- Both in cathode and in anode domain the aspect of the curves is modified, corresponding to the average that simulate solutions/artificial saliva, these being shifted to higher potential values with increasing their pH value.

- Cyclic polarization curves revealed the localized corrosion susceptibility by specific appearance of hysteresis (transpasivity anodic part). The biggest hysteresis was recorded at the tests concerning the Co-Cr alloy in Hank solution, which contains the highest amount of chloride ions.
- By tracing the electrochemical impedance spectroscopy curves it was confirmed the values domain of the polarization resistances obtained for the studied alloy in the tested solutions

Author details

Ion Patrascu[1*], Vlad Gabriel Vasilescu[1] and Stefan Milicescu[1]

*Address all correspondence to: dr.ipatrascu@gmail.com

1 „Carol Davila" University of Medicine and Pharmacy, Bucharest, Romania

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