Corrosion of dental NiCrMo alloys
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Link to publication

Citation for published version (APA):
Muller, A. W. J. (1990). Corrosion of dental NiCrMo alloys
CHAPTER 2

In vitro corrosion rate measurements

2-1 Introduction

The following pages contain three articles on determinations of corrosion rates of dental NiCrMo alloys. The first article describes in detail the two methods used, the 'potentiostatic deaeration method', and chemical analysis of the medium by ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectroscopy). The next article applies the two methods to five dental NiCrMo alloys. In the first two articles a simple medium is used: in order to minimize the chance that electrochemical reactions differing from corrosion reactions would occur, the medium contained only a phosphate buffer and KCl. In the third article the medium has changed. Chemical analysis of the medium is applied to the same alloys, after their immersion in a modified Fusayama artificial saliva [Meyer77] to which thiocyanate has been added, but in which sulphide is absent. Next, the results are given of other mass loss determinations. These results have not been submitted for publication. They mainly concern determinations of the mass loss of Vitallium (a CoCr alloy), and some noble dental alloys, in the modified Fusayama solution mentioned above. Subsequently, a commentary to the articles and results is given. At the end of the chapter a formula for passive alloys similar to the Stern-Geary equation is derived. The limits of applicability of this formula are discussed.

2-2 First article


Measurement of the Small Corrosion Current of a NiCr Alloy by the Potentiostatic Deaeration Method

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Abstract

Postlethwaite's corrosion current measurement method consists of stabilization of the potential of a corroding specimen by a potentiostat, followed by deaeration; the magnitude of the subsequent potentiostat current rise is equated with the corrosion current [Postl81]. In the present study the method was applied to a dental alloy with a low corrosion rate, Micro-Bond N/P. The medium was a 20 mM KCl / 5 mM phosphate buffer solution (pH 7) at 37°C. The measured corrosion current decreased almost inversely with the immersion time, from about 40 nA cm^-2 after five hours to about 0.5 nA cm^-2 after one week. The mass loss of the alloy due to corrosion was determined independently by chemical analysis of the medium (5 ml) of a small corrosion cell. The corrosion current calculated from the mass loss is about 25 nA cm^-2 after five hours after immersion, decreasing to about 2 nA cm^-2 after one week.
Introduction

Measurements of low corrosion rates (less than 0.1 mil yr⁻¹, equivalent to about 200 nA cm⁻²) are considered to be both difficult and tedious to perform with conventional weight-loss or chemical analytical techniques [Fonta83,p.345]. Low rates are measured with electrochemical techniques based on the Stern-Geary equation [Stern57]. Limitations of these electrochemical techniques have been discussed [Gonza85]. One of these limitations, the difficulty in determining Tafel slopes (the slopes must be known to apply the techniques), was our motivation for looking for another electrochemical method to measure the corrosion rates of the alloys we were investigating. The method chosen, the ‘potentiostatic deaeration method’ [Postl81], has to our knowledge not previously been applied to the measurement of small corrosion currents.

Small corrosion currents are present during corrosion of Micro-Bond N/P² in a 5 mM phosphate buffer (pH 7) containing 20 mM KCl at 37°C. Micro-Bond N/P² is a passivating NiCr alloy used in prosthetic dentistry (composition in weight %: 66.15 Ni, 13.5 Cr, 7.5 Ga, 7 Mo, 5 Fe, 0.75 Si). The corrosion rates of nickel-chromium dental alloys are of interest because of possible allergic and toxic reactions in the oral cavity due to their corrosion products [Counc85].

Materials and Methods

FIG. 2.1. The test cell:
(a) plexiglass lid,
(b) cylindrical glass vessel,
(c) glass stirrer,
(d) connection to an electrical motor,
(e) specimen holder,
(f) reference electrode holder,
(g) counter electrode,
(h) gas inlet,
(i) gas outlet,
(j) groove with seal,
(k) heat bath at 37°C.

Cell design. - The test cell for the electrochemical experiments is described in Fig. 2.1. The specimen holder consisted of a G0097 Electrode Holder connected to a K105 Specimen Holder (PAR, New Jersey, USA). The O-rings of the K105 Specimen Holder were greased lightly with silicon grease (Midland Silicones Ltd., Barry, UK). The area of the specimen in contact with the medium was 1 cm². Glued to the lid of the cell was a G0095 Reference Electrode Bridge Tube, containing a K77 Saturated Calomel Reference Electrode (both PAR). A Luggin capillary separated the tube from the medium. The counter electrodes were two G0091 Graphite Rods (PAR). An IKA RE 16 mixing motor (Janke & Kunkel, Staufen, Germany, rotation rate 500 rpm) was connected to the glass stirrer. Silicone rubber stoppers were used throughout. The seal in the lid groove was made of President (Coltène, Switzerland), a vinylpolysiloxane impression material used in dentistry. Air was pumped by a diaphragm pump (Schwarzer Präzision, Essen, Germany). A gas bottle or the air pump was manually connected to the flow rate meter (SHORATE 150, Model 1355 Brooksometer: Emerson, Veenendaal) which led to the gas inlet of the corrosion cell. The gas flow rate was kept at 500 liter hr⁻¹; at this rate the current returned to the baseline within 20 min after the start of reaeration. The purified nitrogen (5.0 quality; 99.999% pure) and the oxygen-nitrogen mixtures (composition: 40, 10, 5, 1 and 0.10 % oxygen) were supplied by Hoekloos (Amsterdam) in gas bottles.
Instrumentation. - Between potentiostatic experiments a Hewlett Packard 34703A voltmeter (input impedance > 10¹⁰ Ω) measured the corrosion potential (E_cor) with respect to the saturated calomel reference electrode. The measured SCE potentials were converted to NHE potentials by adding 241 mV.

The potentiostat was built at the Analytical Chemistry Department of the Free University of Amsterdam as an electrochemical HPLC (High Performance Liquid Chromatography) detector. The potentiostat first amplified the current and then damped it by means of a 1 pole low-pass filter (cutoff frequency 1 Hz). Noise, 'hum', and an offset due to dc leakage currents contribute significantly to the potentiostat signal of a small current (hum: noise at harmonics of the power supply frequency). The offset did not interfere with the current rise measurement. The amplified hum signal, however, can approach the internal supply voltage, giving distortion; for this reason the signal was visually checked by means of an oscilloscope. Distortion of this kind limited the smallest usable input current range to 10⁻¹² - 10⁻¹⁰ nA.

Noise and hum in the potentiostat output signal were suppressed by digital averaging, using a Lab Master analog-digital converter (Scientific Solutions Inc., Ohio, USA), an Olivetti M24 microcomputer, and the READPOTS computer program (written by the authors) that calculated the average of 600 signal values sampled in one minute. This 1 min average was stored on a floppy disk. The resolution of the system at the current range of 10⁻¹² nA was 0.005 nA, i.e. the least significant bit in the 12 bit AD converter signal. The READPOTS program also calibrated the potentiostat by calculating the conversion factors for the various input current ranges after measuring the internal potentiostat calibration currents.

Materials. - Cylindrical specimens (thickness 3 mm, diameter 15.5 mm) of Micro-Board N/P² (Austenal Dental, Chicago, USA) were cast by Tolmejteij's Dental Laboratory (Amhs, The Netherlands). Before immersion a specimen was wet ground to a 600 grit finish, cleaned ultrasonically for 2 min in distilled water, degreased for 2 min first in acetone and then in chloroform, and dried in air.

The medium was a 20 mM KCl / 5 mM phosphate buffer (pH 7) solution. The buffer was made by mixing appropriate amounts of NaH₂PO₄ and K₂HPO₄; the pH, measured at room temperature, was 7.0 ± 0.1. The chemicals were supplied by Merck (pro analysis quality). Between potentiostatic experiments the medium was in free contact with the air but to minimize evaporation no air was bubbled through.

When water loss was perceived, distilled water was added.

Electrochemical techniques. - Fig. 2.2 illustrates the deaeration method [Posd81]. At the corrosion potential (E_cor) the anodic corrosion current (i_anodic) equals the cathodic oxygen reduction current. The potential of the corroding specimen during aeration (E_aeration) is stabilized by a potentiostat. The solution is subsequently purged of oxygen, which causes the cathodic current to disappear. This results in a rise in the potentiostat current equal in magnitude to i_anodic. The solution is aerated after 1 h. A baseline for determining the magnitude of the deaeration current rise is obtained in this study by interpolating the potentiostat currents measured before and after deaeration. During a potentiostatic experiment the potentiostat was connected to the electrodes and set to E_cor. Air bubbling was started. After a delay of 10 min current recording was started (the delay gave a more linear baseline). The current was recorded for 1 h. Then the solution was deaerated for 1 h by purging with pure nitrogen and subsequently aerated again for 1 h. Hereafter current recording and aeration ceased, and the electrodes were reconnected to the voltmeter.

The method for estimating the current rise and the associated error is illustrated in Fig. 2.3.

![Fig. 2.2. Principle of the potentiostatic deaeration method. At the corrosion potential the anodic current balances the cathodic current. During deaeration the cathodic current disappears but the anodic current remains, giving a current rise equal to the anodic corrosion current.](image-url)

![Fig. 2.3. Determination of the current rise and its error. A vertical line v is drawn at 25 minutes after the start of deaeration. A straight line L₁ is drawn through the peaks of the potentiostat current during deaeration and another straight line L₂ through the valleys. The deaeration current is assumed to equal the current at the point D on v halfway between L₁ and L₂. The possible error in D, ε₁, is equated with a quarter of the distance between the intersections of v with L₁ and L₂. Point B lies on v halfway between its intersections with the two extrapolated aeration currents a₁ and a₂. Its possible error ε₂ is equated with half the distance between the intersections of v with a₁ and a₂. The current rise is equated with DB, its error ε with the sum of ε₁ and ε₂.](image-url)
The measured corrosion current was studied as a function of immersion time (t). The first of a series of potentiostatic deaeration experiments was performed a few hours after immersion; the subsequent experiments took place one, two, four, and six days later.

Some other types of potentiostatic experiments were also performed:
1. The influence of variable partial pressure of oxygen (pO2) on the potentiostatic current was investigated. It follows from Eq. [3.3.14] in [Bard80] that the cathodic current \( i_c \) due to a redox couple, at a potential \( V \) far below its equilibrium potential \( E_{eq} \) can be described by:

\[
\dot{i}_c = \dot{i}_{c,0} e^{rac{V - E_{eq}}{\beta_c}}
\]  
(2-1),

where \( \beta_c \) equals the Tafel constant of the current, \( c \) the concentration of the oxidizer, and \( \dot{i}_{c,0} \) a constant independent of \( c \) and \( V \). According to Henry's Law the concentration of oxygen in solution is proportional to \( pO_2 \). Hence one can write

\[
\dot{i}_c = \dot{i}_{c,0} \beta_H pO_2
\]  
(2-2),

in which \( \beta_H \) is Henry's constant for oxygen in water. \( E_{eq} \) depends on \( pO_2 \); an expression for \( E_{eq} \) follows from the reaction equation:

\[
O_2 + 4H^+ + 4e^- \rightarrow 2H_2O
\]

Hence:

\[
E_{eq} = E_0 + \frac{RT \ln [pO_2]}{4F} + \frac{4F}{2.303RT} \log pO_2
\]  
(2-3)

\[
E_{eq} = E_0' + 0.015 \log pO_2
\]  
(2-4)

where \( E_0' \) equals the sum of the first two terms in Eq. (2-3).

Substituting Eq. (2-4) in Eq. (2-2) gives:

\[
\dot{i}_c = \dot{i}_{c,0} \beta_H pO_2 10^{-\frac{V - E_{eq}}{\beta_c}}
\]  
(2-5)

A typical value of \( \beta_c \) is 0.12, but lower values have also been found [Horrace68]. This gives for the expected exponent of \( pO_2 \) in Eq. (2-5) a value of 1.13 or higher.

Because of this almost linear dependency between the cathodic current and \( pO_2 \) the current was expected to disappear quickly after purging with pure \( N_2 \). As a check on the dependency nitrogen-oxygen mixtures with varying \( pO_2 \) were bubbled through the medium: 1, 5, 10%, oxygen, air (20.95%, oxygen), and 40% oxygen (Fig. 2.6).

In Fig. 2.6 the curve of the 1 min averages was smoothed by three-point averaging twenty times. Three-point averaging consisted of replacing each nth 1 min average by the average, with weight factors of 0.14/1, 0.12/1 and 0.14/14, of the \( n-1 \)th, \( n \)th and \( n+1 \)th 1 min averages. The smoothed curve is indicated by the broken line.
Inductively Coupled Plasma - Atomic Emission Spectroscopy) at the Analytical Chemistry Department of the University of Amsterdam. Detection limits were 5 ppb for Ni, Cr and Fe, 40 ppb for Mo, and 50 ppb for Ga. From the measured concentrations a corrosion current was calculated by the method described in the Appendix.

The CURVFIT program (written by the authors) fitted log $i_{\text{cor}}$ vs log $t$, and log $c$ vs log $t$, by the method of weighted least squares [DeLev86] to the relations:

$$\log i_{\text{cor}}(t) = a \log t + b,$$
$$\log c(t) = a \log t + b,$$

which are equivalent to:

$$i_{\text{cor}}(t) = i_0 t^a$$
$$c(t) = c_0 t^a$$

where $i_0$ and $c_0$ equal $10^b$. The weight factors were obtained by taking the inverse square of the errors $e$ (Fig.2.3).

Results
A change in stirring rate or gas flow rate intermittently influenced the measured $E_{\text{cor}}$ during corrosion potential measurements and the measured current during potentiostatic experiments. On one occasion, for instance, turning the mixer motor off caused the measured $E_{\text{cor}}$ to drop about 20 mV in 10 min; turning the motor on again caused the $E_{\text{cor}}$ to increase 10 mV in 10 min. Hence, care was taken to keep the stirring rate and gas flow rate constant, especially while changing gases.

During potentiostatic experiments the averaged measured currents of consecutive minutes often differed less than 0.01 nA.

The effect upon the potentiostatic current of bubbling nitrogen with varying $p_{O_2}$ content through the medium is illustrated in Fig. 2.6 (the peak inside the 1% $p_{O_2}$ valley is attributed to a temporary decrease of the gas flow rate).

Ten minutes were sufficient to stabilize the potentiostatic current after a change of $p_{O_2}$. The difference between the potentiostatic current during purging with $N_2$, and with an $O_2 / N_2$ mixture is associated with the cathodic current $i_c$. This current is plotted vs $p_{O_2}$ on a log-log plot in Fig. 2.7: a straight line is obtained, and the CURVFIT program yielded a value of 0.832 for the exponent of $p_{O_2}$.
The curve obtained during a potentiostatic deaeration experiment deviated from the one in Fig. 2.2. The curve consisted of an 'initial rise' that ended within 20 min, and a 'secondary rise' that started after about 60 min (Fig. 2.8).

After a voltage step of 70 mV the initial rise decreased from 2.0 to 1.2 nA cm\(^{-2}\), while the secondary rise increased from 0.6 to 1.2 nA cm\(^{-2}\) (Fig. 2.9); hence the secondary rise is anodic.

Further investigation of the secondary rise by varying \(p_O_2\) in the purging gas between 0.10 % and zero showed that 0.10 % oxygen sufficed to inhibit the secondary rise (Fig. 2.10).

Fig. 2.11 gives \(E_{cor}\) vs log \(t\) for three runs. After immersion \(E_{cor}\) decreased at first, reached a minimum at about 1000 s, and then rose linearly with log \(t\).

Fig. 2.12. Results of run 1 of potentiostatic experiments. Currents have been divided or multiplied by the indicated factors and have been displaced vertically for clarity. The indicated corrosion current values and their errors have been obtained by the method illustrated in Fig. 2.3.

Fig. 2.13. Results of run 2 of potentiostatic experiments.
Figs 2.12-14 give the results of the potentiostatic experiments of three runs; \( i_{\text{cor}} \) values were obtained from these figures by the method described in Fig. 2.3. For larger immersion times \((t > 100 \text{ h})\) the main source of error in \( i_{\text{cor}} \) was given by the \( e_2 \) term (Fig.2.3): the potentiostat current during reaeration tended to remain higher than its pre-deaeration value.

After plotting \( \log i_{\text{cor}} \) vs \( \log t \) straight lines could be drawn through the points (Fig.2.15). The corrosion current as a function of time can consequently be written as Eq. (2-6a). The CURVFIT program yielded for \( i_0 \) values of resp. 209, 158 and 290 nA cm\(^{-2}\) hour\(^{-1}\), and for \( a \) values of resp. -1,12, -1,02, and -1,15, for the three runs.

Only nickel and iron concentrations were measurable during chemical analysis of the medium of the test cell for mass loss determinations. Molybdenum could be detected in two cells, at its detection limit. No chromium or gallium was detected. The iron concentration was about 20 ppb and independent of the immersion time. The nickel concentration increased with the immersion time, and was linear on a log \( c \) vs log \( t \) plot (Fig.2.16). The nickel concentration as a function of immersion time can consequently be written as:

\[
c(t) = c_0 t^a
\]

(2-7).

The CURVFIT program yielded values of 77,6 for \( c_0 \) and 0,261 for \( a \) (\( t \) in hours). From these values the following corrosion current was obtained (see the Appendix):

\[
i_{\text{cor}}(t) = 69.7 h^{-0.739} [\text{nA cm}^{-2}]\]

This current is depicted in Fig. 2.15 and can be seen to be in good agreement with the currents obtained by the potentiostatic experiments, especially at an immersion time of 24 h; the current decreases with a somewhat smaller slope than the currents obtained from the potentiostatic experiments.
Discussion

The results. - An influence of stirring rate upon the measured potentials of a reference electrode with a porous plug as liquid junction has been described previously [Illin81, Brezi83]. The influence of stirring rate and gas flow rate found in this study is attributed to the same effect occurring in the Luggin capillary. The influence could be eliminated by keeping the stirring rate and gas flow rate constant and for this reason it was not further investigated.

Figs 2.6 and 2.7 show that $i_o$ is indeed almost linearly dependent on $pO_2$. Hence extrapolation of $i_o$ to a $pO_2$ value zero results in the value zero and it follows that small amounts of oxygen probably do not cause a significant cathodic current. For this reason it was assumed that there was no need to purify the purging gas of traces of oxygen.

It is pointed out in the Materials and Methods section that the exponent of $pO_2$ was expected to be larger than 1,13. Instead a value of 0,832 was found. Hence equations (2-1) and (2-5) do not adequately describe the kinetics of oxygen reduction in our experiments.

The initial rise is attributed to the disappearance of the cathodic oxygen reduction current. The secondary rise can be explained by an anodic mechanism and by a cathodic mechanism (Fig.2.4). The anodic mechanism is slow depassivation: it is assumed that oxygen stabilizes passivation, as follows from the oxygen adsorption theory of passivation [Uhlig79]. The cathodic mechanism is a slowly decreasing cathodic current due to slow depletion (by desorption or reduction) of adsorbed oxygen. The presence of such a cathodic current ($i_{ad}$) would imply that the initial rise is lower than the corrosion current by an amount $i_{ad}$ (Fig.2.17). However, the secondary rise is anodic (Fig.2.9), hence it cannot be explained by the reduction of slowly depleted adsorbed oxygen. Consequently the secondary rise supports the view that oxygen plays a role during passivation by inhibiting the anodic current. It is known that small amounts of oxygen can inhibit the corrosion of some passivating alloys [Covin86].

The late appearance of the secondary rise can be explained by: (i) slow desorption or slow reduction of adsorbed oxygen that is causing inhibition of the anodic current, or, (ii) the existence of a critical oxygen concentration for the inhibition of the anodic current. Only after prolonged deaeration would the oxygen concentration drop below this critical concentration.

An $E_{cor}$ vs $t$ curve, on a time scale of 0 - 12 h, of Micro-Bond Ni/P2 in an artificial saliva (pH 3,65-4, 37°C) has been published previously [Meyer77]. When replotted $vs$ log $t$ this curve becomes a straight line having the same slope as the curves in Fig. 2.11 but lying 250 mV higher. This curve showed no initial decrease.

Linear $log i$ vs log $t$ curves resembling Fig. 2.15 have been obtained during potentiostatic experiments on passivating alloys such as 18Cr-8Ni stainless steels and during scratching experiments with these alloys [Burst83a,84]. In neutral and alkaline mediums the exponent of $t$ in these experiments is about 1 as well [Kirch87]. It is emphasized that the results pictured in Fig. 2.15 have been obtained under conditions differing from the experiments described in [Burst83a,84], as the potential at which our potentiostatic experiments were performed was different for each experiment.

The shapes of the $i_{cor}$ vs $t$ curves of the three runs in Fig. 2.15 are quite similar. However, there is a substantial difference between the corrosion currents of the distinct runs, the corrosion current of run 3 being twice the corrosion current of run 2. The cause of this variability is not known.

For a Ni20Cr10Mo alloy (which composition resembles the composition of Micro-Bond Ni/P2) a mass loss by corrosion of 4 µg cm$^{-2}$ has been given for an immersion time of one week at pH 7 [Geis-88]. From Eq. (2-7) a mass loss is calculated for the same period of 1,5 µg cm$^{-2}$, which has the same magnitude.

The current calculated from the potentiostatic deaeration method and the current calculated from the mass loss do not necessarily have to be the same. Chemical analysis of the medium yields the matter entering the medium, whereas the electrochemical method yields the matter entering the passive layer. If, for instance, the thickness of the passive layer increases, then the 'electrochemical current' would be larger than the 'mass loss current'. In the present case the mass loss current seemed to be larger than the electrochemical current for immersion times longer than 24 hours, suggesting that the thickness of the passive layer decreases with longer immersion times.
The potentiostatic desorption method - The method allows the measurement of very small corrosion currents (about 1 nA cm⁻²) in a simple and straightforward way, with minimal disturbance (Fig. 2.15); below 1 nA cm⁻² the measuring error increases rapidly with decreasing tcorr (Fig. 2.15).

One advantage of the method is that the corrosion current is measured directly [Postl 81]. A second advantage is the absence of potential scanning during measurement. Potential scanning may cause charging of ions inside the passive layer, and the associated current may mask the anodic and cathodic currents that occur during corrosion. The corroding specimen is minimally disturbed by the method. One can consequently perform a series of measurements on a single specimen, enabling a more accurate determination of the corrosion current as a function of time, as the specimen particularity can be separated from other causes of variability.

The measuring system yields 1 min averages: fluctuations containing frequencies larger than about 16 mHz (1 / 60 s) are averaged out. If these fluctuations have the nature of noise [Hladk 82, Seral 86] then they constitute a background normally resulting in inaccurate measurement of the potentiostat current; the high repeatability of the 1 min averaged currents can be attributed to this background-noise suppression. If the fluctuations are caused by cyclic electrochemical processes then their removal is a disadvantage. However, the READPOTS computer program can easily be adapted to perform signal analysis of the potentiostat signal, e.g. the determination of the power spectrum of higher frequency components. This would allow the detection of cyclic processes during measurement.

The main disadvantage of applying the method to the measurement of small corrosion currents is the uncertainty concerning interference by adsorbed oxygen (Fig. 2.17). To give interference, adsorbed oxygen should not be desorbed during desorption, and its reduction rate should be neither too low nor too high. If its reduction rate is very low, i_ads is very small; if its reduction rate is very high, i_ads is very high at first but then decays rapidly as the adsorbed oxygen is depleted. We have no evidence of the presence of oxygen irreversibly adsorbed to Micro-Bond N/P², nor evidence concerning its reduction rate.

Some noble metals (Pd, Pt, Rh, Ir, Ru, but not Au) can chemisorb oxygen reduction equivalents of 100 to 500 μC cm⁻² [Bockr 69]; note that these metals are not present in Micro-Bond N/P². If an amount of 100 μC cm⁻² is reduced in one hour this results in an i_ads of about 27 nA cm⁻², which has the same magnitude as the initial rise measured in this study. Large coverage with adsorbed oxygen is associated in the case of noble metals with large cathodic oxygen reduction currents at low potential [Bockr 69]. From unpublished potentiodynamic experiments it follows that the cathodic oxygen reduction current of Micro-Bond N/P² is small at about 0 mV. This makes a large coverage of the alloy by adsorbed oxygen less plausible. Nevertheless, the presence of a significant i_ads during desorption cannot be ruled out.

The determined corrosion current of Micro-Bond N/P² was very low and was found to decrease with the immersion time according to Eq. (2-6a). The alloy seemed to depassivate slowly in the absence of oxygen.

The accordance of the measured corrosion current and the corrosion current calculated from chemical analysis data establishes the validity of the potentiostatic desorption method.

Acknowledgements
The authors wish to thank Tolmeijer’s Dental Laboratorium (Arnhem) for casting the specimens of Micro-Bond N/P², Pim Voogt of the Analytical Chemistry Department of the Free University of Amsterdam for lending the potentiostat, Hans Balke of the Analytical Chemistry Department of the University of Amsterdam for the ICP-AES determinations, Mr. H.M. Nieuwenhuijs for his assistance in all matters concerning gas and gas bottles, prof. F.P. Jsseling of the Corrosion Laboratory of the Royal Netherlands Naval College for referring us to the article of J. Postelthwaite and Jeanne Kruchowski for proofreading countless versions of this article.

The University of Amsterdam assisted in meeting the publication costs of this article.

Appendix
The CURVFIT program yields as best fit for the concentration of nickel as a function of immersion time:

\[
\begin{align*}
\epsilon (t) &= \epsilon_0 + \epsilon_1 t + \epsilon_2 t^2 \\
&= \epsilon_0 + \epsilon_1 \frac{b^2}{a} + \epsilon_2 \frac{b^3}{a^2}
\end{align*}
\]

where \( a = \frac{b^2}{3600} \), \( b \) is the solution time in seconds, and \( \epsilon_0, \epsilon_1, \epsilon_2 \) are parameters.

The function \( \frac{d \epsilon(t)}{dt} \) then equals:

\[
\frac{d \epsilon(t)}{dt} = \epsilon_1 a - \epsilon_0 \frac{b}{3600}
\]

The associated corrosion current follows from:

\[
\text{Corrosion current} = A S \frac{\epsilon_0}{3600} \frac{\epsilon_1 a}{3600} \frac{b}{3600} = A S \frac{\epsilon_0 \epsilon_1 a}{3600^2}
\]

where \( A \) is the surface area of the corroding specimen (1.327 cm²), and \( S \) is the weight of the medium (5.00 g).

Substitution gives:

\[
\epsilon_0 = 69.7 \times 10^{-12} \text{[nA cm}^{-2}]\text{].}
\]
The corrosion rates of five dental NiCrMo alloys determined by chemical analysis of the medium using ICP-AES, and by the potentiostatic deaeration method

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Abstract
The corrosion rates of five dental NiCrMo alloys in a 20 mM KCl/5 mM phosphate buffer (pH 7) were determined by chemical analysis of the medium and by the potentiostatic deaeration method. The corrosion current of four alloys decreased almost inversely proportional with time, reaching values in the range 0.1 - 10 nA/cm² after one week. The corrosion current of the alloy with the lowest molybdenum content (4%) showed an initial decrease as well, but started to rise after one day, reaching a value of 25 nA/cm² after one week. A linear relation was found between the $E_{corr}$ and $\log (i_{corr})$ of all the alloys for the entire immersion time.

Introduction
As nickel and chromium are known allergens and carcinogens [Counc85], the corrosion rates of dental NiCrMo alloys are of interest. The corrosion current, a measure of the corrosion rate, can be obtained by the polarization resistance method, which calculates the current from Tafel slopes and polarization resistance by means of the Stern-Geary equation [Stern57]. However, the results of this method do not always agree with the results of mass loss experiments [Callo76]. Several causes of this limited applicability have been given [Gonz85]. In the case of nickel submerged in sea water the method underestimated the corrosion rates compared to weight loss by an order of magnitude [Callo76]. In unpublished potentiodynamic investigations of NiCrMo alloys the polarization resistance method could not be applied: it was impossible to obtain Tafel slopes due to the nonlinearity of the anodic and cathodic branches of the potentiodynamic curve on a log $i$ vs $E$ plot. In addition, the shape of the potentiodynamic curve of dental NiCrMo alloys depends on the scanning rate [Geis-87a], which cannot be reconciled with the assumptions made by Stern and Geary in their derivation of the Stern-Geary equation.

These difficulties were the motivation for measuring the corrosion rates of NiCrMo alloys by two other methods instead, chemical analysis of the medium and the potentiostatic deaeration method. The latter method measures the corrosion current directly: a potentiostat maintains the specimen potential measured in the presence of oxygen, i.e. the corrosion potential; the corrosion current is equated with the potentiostat current after oxygen removal [Postl81, Mull89a]. Recently the two methods have been applied to the measurement of the corrosion rate of Micro-Bond N/P² in a 5 mM phosphate (pH 7) and 20 mM KCl solution (37°C) [Mulle89a]. Good agreement was found between the corrosion currents obtained by these methods. The present study extends these investigations to five other dental NiCrMo alloys. Because the experimental data are evaluated in this study in a slightly different way, the data from the previous study are re-evaluated as well. The composition of the alloys is given in Table 2-7. Hereafter the abbreviations CER, W77, NP2, FOR, RES and W88, are used for Ceramalloy II, Wiron 77, Micro-Bond N/P², Forte, Resistal P, and Wiron 88.
TABLE 2.1. TRADE MARK, MANUFACTURER, AND COMPOSITION (%) OF THE INVESTIGATED Ni-Cr-Mo ALLOYS ARRANGED ACCORDING TO INCREASED Mo-CONTENT. X INDICATES AN UNCERTAIN PERCENTAGE OF ACCOMPANYING ELEMENTS; THE CONTENT OF WHICH IS GENERALLY SMALLER THAN 1 %.

<table>
<thead>
<tr>
<th>Trade Mark</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Others</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramalloy II</td>
<td>73</td>
<td>18</td>
<td>4</td>
<td>Si, B 1</td>
<td>[Schoe84]</td>
</tr>
<tr>
<td>(Johnson &amp; Johnson)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wiron77</td>
<td>70</td>
<td>20</td>
<td>6</td>
<td>Si, Ce, B X</td>
<td>[Forsch86]</td>
</tr>
<tr>
<td>(Bego)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Micro-Bond N/P²</td>
<td>66.15</td>
<td>13.5</td>
<td>7</td>
<td>Ga, 7,5, Fe, 5, Si</td>
<td>[Forsch86]</td>
</tr>
<tr>
<td>(Howmedica)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Force</td>
<td>63</td>
<td>21.5</td>
<td>8</td>
<td>Ta, 3,8, Fe, 1,</td>
<td>[Forsch86]</td>
</tr>
<tr>
<td>(Unicera)</td>
<td></td>
<td></td>
<td></td>
<td>Si, Cr, Mn, Al X</td>
<td>[Schoe84]</td>
</tr>
<tr>
<td>Recital P</td>
<td>64</td>
<td>21</td>
<td>9</td>
<td>Nb 4</td>
<td>[Forsch86]</td>
</tr>
<tr>
<td>(Degussa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wiron88</td>
<td>64</td>
<td>21</td>
<td>10</td>
<td>Si, Ce X</td>
<td>[Forsch86]</td>
</tr>
<tr>
<td>(Bego)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE 2.2. ANALYSIS LINES USED AND CORRESPONDING CONCENTRATION AND MASS LOSS DETECTION LIMITS.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce II</td>
<td>238.892</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>Cr II</td>
<td>267.716</td>
<td>4</td>
<td>15</td>
</tr>
<tr>
<td>Fe II</td>
<td>238.204</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>Ga I</td>
<td>294.364</td>
<td>10</td>
<td>151</td>
</tr>
<tr>
<td>Mo II</td>
<td>281.615</td>
<td>5</td>
<td>19</td>
</tr>
<tr>
<td>Nb II</td>
<td>316.340</td>
<td>20</td>
<td>75</td>
</tr>
<tr>
<td>Ni I</td>
<td>341.480</td>
<td>6</td>
<td>23</td>
</tr>
<tr>
<td>Si I</td>
<td>251.611</td>
<td>10</td>
<td>38</td>
</tr>
</tbody>
</table>

*) I: atomic; II ionic

For a medium volume of 5 ml, medium weight 5,000 g, corroding surface area 1,327 cm².

TABLE 2.3. EXPERIMENTAL CONDITIONS SELECTED FOR THE SIMULTANEOUS DETERMINATION OF THE ANALYSIS OF INTEREST.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner gas (Ar) flow rate</td>
<td>0.7 l min⁻¹</td>
</tr>
<tr>
<td>Outer gas (Ar) flow rate</td>
<td>15 l min⁻¹</td>
</tr>
<tr>
<td>Solution uptake rate</td>
<td>1.5 ml min⁻¹</td>
</tr>
<tr>
<td>Power input to the plasma</td>
<td>1.1 kW</td>
</tr>
<tr>
<td>Thickness of the observed plasma layer</td>
<td>1.05 mm</td>
</tr>
<tr>
<td>Observation height in the plasma</td>
<td>17 mm</td>
</tr>
</tbody>
</table>

*) above top of induction coil

Materials and Methods

Cylindrical specimens (thickness 3 mm, diameter 15.5 mm) of the alloys W77, W88, FOR, and CER were cast by Amsterdams Tandtechnisch Laboratorium BV (Amsterdam). The RES specimen was kindly provided by Degussa (The Hague). All alloys were investigated in the as-cast condition. Prior to the mass loss and potentiostatic deaeration experiments the specimens were wet ground to a 600 grit finish, ultrasonically cleaned for 2 min in distilled water, and degreased by placing it for 2 min in acetone and in chloroform.

Mass loss determination

The test cell for the chemical analysis experiments (Fig.2.18) differed slightly from the one in the previous study, in which the specimen was pressed onto a silicon ring by means of a screwcap. The early cell leaked frequently, which was attributed to shifting of the specimen with respect to the silicon ring while being screwed shut. To avoid shifting a metal spring was used instead to press the specimen against the silicon ring.

FIG. 2.18. Test cell arrangement for mass loss determination:
(a) glass bottle, (b) silicon rubber ring, slightly greased with silicon grease, (c) the specimen, (d) metal spring, (e) position where an elastic band is wrapped around the spring.

Immersion was terminated by removal of the specimen. Immersion times were 1, 3, 8 h and 1, 3 and 7 days. For each alloy and immersion time three cells were prepared. For some alloys a few additional cells were prepared.

The concentrations (c) of Ni, Cr, Mo, and Fe were determined in all cells. CER, FOR, and RES, and some W77 and W88 cells were analyzed for the presence of Si. The NP2, FOR and RES cells with the longest immersion times were analyzed for the presence of Nb and, in the case of NP2, for the presence of Ga. The applied analytical method was Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES). The instrument used was a Jarrell-Ash Atomcomp model 970 ICAP multipchannel spectrometer. The main characteristics of the instrumental facilities have been specified elsewhere [Maess82]. Samples were brought into the plasma by means of a cross flow nebulizer [Maess84] fed by a ten roller peristaltic pump (Minipuls, Gilson Medical Electronics, France). A sample volume of 4 ml sufficed to execute two independent series of measurements of the elements of interest. The analysis lines corresponding to the optical channels simultaneously used are listed in Table 2.2 together with the detection limits; applied experimental conditions are summarized in Table 2.3. The relative standard deviation of a single analyte determination ranged from 2 % for Ni to 5 % for Si. The results show (see the Discussion) that only minor amounts of elements other than nickel were released. In the rests of this section it is therefore assumed that only nickel entered the medium.

From the measured concentrations (ppb) a mass loss (m) in (ng/cm²) was calculated according to

\[ m = \text{Ref.} \]

where \( \text{Ref.} \) is the weight of the medium (5,000 g) and \( S \) is the surface area of the corroding specimen (1,327 cm²).
On a log-log plot the cumulative mass loss vs immersion time gave curves resembling straight lines. In order to check this observation the data were fitted to the equation

\[ \log m = a + \frac{b}{h} + c \frac{t}{d} \]

where \( u = \log h \) (hours), the immersion time; deviation from a straight line would result in a large value for \( c \). The graph of CER strongly deviated from a straight line. Its data were fitted to a third degree polynomial in \( u \):

\[ \log m = a + b + c u + d u^2 + e u^3 \]

The coefficients \( a, b, c, d \) and \( e \) were calculated by the GraphPAD program (ISI Software, Philadelphia, PA, USA).

It follows from equation (2-9) that

\[ \frac{dm}{dt} = \frac{1}{600} \frac{dt}{db} \]

Also,

\[ \frac{dm}{dt} = \frac{1}{600} \frac{dt}{db} \]

The corrosion current equals:

\[ i_{\text{cor}} = \frac{zF}{A} \frac{dm}{dt} \]

where \( z \) is the valence of nickel, \( A \) its atomic weight and \( F \) the Faraday constant.

### The potentiostatic deaeration method

The method is depicted in Fig. 2.19. At the corrosion potential \( (E_{\text{cor}}) \) the anodic corrosion current \( (i_{\text{cor}}) \) equals the cathodic oxygen reduction current \( [\text{Wagne38}] \). The potential of the corroding specimen during aeration is first stabilized by connecting the specimen to a potentiostat set at this potential. Next, the cathodic current is made to disappear by purging the medium of oxygen by bubbling nitrogen. The anodic corrosion current remains, resulting in a rise in the potentiostatic current equal to \( i_{\text{cor}} \). The solution is aerated again after 1 hour. A baseline for determining the corrosion current and its deviation from a straight line was obtained by interpolating the potentiostat currents measured before and after deaeration. The corrosion current is measured a few hours after immersion, and 1, 2, 4, and 6 or 7 days later. In the present study these runs of experiments were done in duplicate for each alloy.

![FIG. 2.19. Principle of the potentiostatic deaeration method. At the corrosion potential the anodic current balances the cathodic current. During deaeration the cathodic current disappears but the anodic current remains, giving a current rise equal to the anodic corrosion current.](image)

The measuring system consisted of a test cell, a voltmeter, a potentiostat, an ADDA converter and a microcomputer. The test cell was a cylindrical glass vessel, containing 1 L of the medium, a 20 mM KC1/5 mM phosphate buffer, made by adding to distilled water appropriate amounts of KCl, NaH₂PO₄ and KH₂PO₄, all obtained from Merck. In contact with the medium were a KHS specimen holder (PAR, Princeton, NJ, USA); two counter electrodes (G0091 graphite node PAR), a G0095 reference electrode bridge (PAR), containing a K77 saturated calomel reference electrode (PAR) and a glass stirrer. The flow rate of the gas (air or purified nitrogen) was kept at 500 L h⁻¹. The purified nitrogen was 3.0 quality: 99.999% pure (Hoekloos, Amsterdam). A Hewlett Packard 5470A voltmeter was used to measure the potential of the specimens between potentiostatic experiments. The potentiostat was a HP8901B detector built at the Analytical Chemistry Department of the Free University of Amsterdam. It was connected to the input of an ADDA converter present in a Lab Master board (Scientific Solutions Inc., OH, USA); this board was placed in an Olivetti M 24 microcomputer. The READPOTS program, written by the authors, calculated and stored on floppy disk the average of 600 signal samples taken in one minute. After a potentiostatic experiment these one-minute averages were plotted vs time. In the present study these averages were subjected to subsequent digital averaging by three-point averaging three times. Three-point averaging consisted in replacing an nth one-minute average \( I_n \) by \( \bar{I}_n \) calculated from

\[ \bar{I}_n = \frac{1}{4} \left( X_{n-1} + 2 X_n + X_{n+1} \right) \]

The transfer function \( H(\omega) \) describes the effect in the frequency domain of digital averaging [Hammi77] (\( \omega \) is the angular frequency). The three-point averaging described by equation (2-13) has a transfer function \( H(\omega) \) [Hammi77, p. 52]:

\[ H(\omega) = \frac{1 + \cos(\omega/2)}{2} \]

The transfer function \( H(\omega) \) of three times averaging is:

\[ H(\omega) = H(\omega)^3 = \left( \frac{1 + \cos(\omega/2)}{3} \right)^3 \]

Such averaging is equivalent to passing the data through a low-pass filter with a cut-off frequency (-3 dB point) of 1 / (9 min). The potentiostat vs time curves obtained from data smoothed in this way were used to determine the corrosion current and its error in the same manner as in the previous study [Mulle89a].
Results

Nickel determinations
- Nickel was detected in all 118 cells. In Figs 2.20-21 the calculated nickel loss is plotted vs the immersion time. Nickel concentrations found after one week immersion ranged from 108 ppb (FOR) to 1161 ppb (CER). Table 2.4 lists the values calculated by the GraphPAD program for the coefficients of \( a \) in Eqs (2-9) from the mass loss data. The product of \( e \) and 2.2 (= log 170, the longest immersion time) is much smaller than \( b \), except in the case of CER. This shows that the deviation from a straight line is small. The fitting curves in Figs. 2.20 and 2.21 have been calculated from the coefficients in Table 2.4.

Chromium was detected in 25 % of the cells. The concentration seemed to increase with the immersion time. The highest value found was 9 ppb (W77; one week immersion). Molybdenum was detected in only two cells (both NP2), at a concentration near its detection limit. Iron was detected in 56 % of the cells. Its concentration seemed to increase with the immersion time. The largest concentration found was 32 ppb (NP2; 23 h immersion). Most values were about 10 ppb. In the case of NP2 the average value was 16 ppb, and the concentration did not clearly increase with immersion time. Silicon determinations were carried out in 68 cells. In all determinations silicon was detected. Concentrations ranged from 0.1 to 2.3 ppm (CER; 22 h immersion). After one week immersion no niobium was detected in cells of NP2, FOR and RES and no gallium in NP2 cells. Other cells of these alloys were not further analyzed for these elements.

Table 2.4. Calculated values for the coefficients \( a, b, c \) and \( d \) in Eqs (2-4) and (2-5).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>( a )</th>
<th>( b )</th>
<th>( c )</th>
<th>( d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramalloy II</td>
<td>2.2488</td>
<td>0.6170</td>
<td>-0.3016</td>
<td>0.1388</td>
</tr>
<tr>
<td>Wiron 77</td>
<td>2.2742</td>
<td>0.8944</td>
<td>0.0469</td>
<td>0.0024</td>
</tr>
<tr>
<td>Micro-Bond N/P2</td>
<td>2.4979</td>
<td>0.1528</td>
<td>0.0359</td>
<td>0.0024</td>
</tr>
<tr>
<td>Unitek-Forte</td>
<td>2.1317</td>
<td>0.3418</td>
<td>-0.0486</td>
<td>0.0138</td>
</tr>
<tr>
<td>Resistal P</td>
<td>2.2597</td>
<td>0.2319</td>
<td>-0.0136</td>
<td>0.02319</td>
</tr>
<tr>
<td>Wiron 88</td>
<td>2.0166</td>
<td>0.2347</td>
<td>0.02319</td>
<td></td>
</tr>
</tbody>
</table>

The potentiostatic deaeration method.
Figs 2.22 and 2.23 give \( E_{\text{corr}} \) vs \( \log t \) for all runs.

FIG. 2.20. Mass loss vs immersion time for W77, NP2, and W88.

FIG. 2.21. Mass loss vs immersion time for CER, RES, and FOR.

FIG. 2.22. Corrosion potential vs immersion time for Wiron 77, Micro-Bond N/P2, and Wiron 88. The labels W77 and W88 have inadvertently been switched.

FIG. 2.23. Corrosion potential vs immersion time for Ceramalloy II, Resistal P, and Forte.

88
Figs 2.24-26 give the results of the potentiostatic experiments of runs of W88, W77 and CER. The other runs gave similar graphs.

Mass loss determinations

Mass loss of nickel increased with the immersion time, and was almost linear on a log m vs log t plot (Figs 2.20 and 2.21), with the exception of CER. The nickel loss after one week ranged from about 0.45 µg/cm² (W88, RES, FOR) to 4.3 µg/cm² (CER). This range comprises most of the previously published values of nickel loss by dental NiCrMo alloys (Table 2.5). There is not much difference between the nickel losses of RES and FOR, alloys with almost identical content of Ni, Cr, and Mo (Table 2.1). All curves resemble straight lines except the CER curve, which clearly bends upwards. It follows from Table 2.4 that the time dependency of the nickel loss can be described as \( m = kt^b \), where \( b \) equals the immersion time, and with \( b \) equal to 0.38, 0.15, 0.34, 0.23 and 0.22, for W77, NP2, FOR, RES and W88.

The data of Geis-Gerstorfer et al. (1987a) on the nickel loss of NP2, W88 and Elite (Ni51,5Cr7,5Mo7,5 Nb0,8Si0,42 Mn0,35 Co0,21 Fe) in 0.1 M lactic acid - 0.1 M NaCl (pH 2,3) were replotted on a log-log plot and yielded straight lines for the

<table>
<thead>
<tr>
<th>Alloy (including Ni, Cr, Mo and Nb content)</th>
<th>Mass loss after one week [µg/cm²]</th>
<th>Calculation method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wiron S (72Ni10Cr4,7Mo)</td>
<td>modified Fusayama</td>
<td>5.0</td>
<td>[Espe78]</td>
</tr>
<tr>
<td>artificiwal saliva (pH ca 5)</td>
<td>interpolation of data from a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-months experiment</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biobond (79Ni13CrMo)</td>
<td>autoclaved saliva</td>
<td>4.1</td>
<td>[Newm81]</td>
</tr>
<tr>
<td>Unibond Fonté (63Ni12Cr8Mo)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Astro Superior (66Ni12Cr2Mo)</td>
<td>autoclaved saliva</td>
<td>0.33</td>
<td>[Covi85]</td>
</tr>
<tr>
<td>(brought to pH 2 and 6)</td>
<td>interpolation of data from a</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>Ceramalloy (72Ni19Cr4Mo)</td>
<td></td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>Ceramalloy II (72Ni19Cr4Mo)</td>
<td></td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>Wiron 8</td>
<td></td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>0.1 M NaCl</td>
<td></td>
<td></td>
<td>[Geis-87a]</td>
</tr>
<tr>
<td>0.1 M lactic acid (pH 2.3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Micro-Bond NiF² (67Ni12Cr7Mo)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aldident Elite (64Ni21Cr9Mo3Nb)</td>
<td>pH 3</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>pH 7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80Ni120Cr</td>
<td>not specified</td>
<td>3.4</td>
<td>[Geis-88]</td>
</tr>
<tr>
<td>70Ni120Cr10Mo</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.5 RESULTS OF EARLIER DETERMINATIONS OF NICKEL LOSS BY DENTAL Ni-Cr-Mo ALLOYS.
first two alloys; in the case of Elite the fit was less good. The time dependency of the nickel loss in their study can be written as $b^t$, where $b$ equals 0.26, 0.10 and about 0.10 for NP2, W88 and Elite. These values for $b$ are similar to the values of $b$ in Table 2.4.

Covington et al. (1985) have found a linear relation between the mass loss of nickel and the immersion time in their experiments, which lasted 30 or 120 days. Some of their mass loss vs time curves are slightly convex: replottting the pH 2 and 4 data in their Fig. 1 on log-log plots yielded straight lines and gave values for $b$ of 0.78 and 0.81 respectively, values much larger than ours. Their findings are consequently in contrast to our results.

There is widespread scattering around the fitting curves in Figs 2.20 and 2.21; for instance, the mass losses of NP2 at 72 hours are 635, 690, 763 and 894 ng Ni/cm², and the losses of FOR at 7 days immersion 407, 414 and 757 ng Ni/cm². This scattering cannot be attributed to imprecision of the ICP-AES measuring method, which is 2% (see Materials and Methods), but is attributed to specimen peculiarity instead.

Silicon was found in all cells, including cells of RES, which does not contain silicon, and is therefore attributed to dissolved silicon grease (this grease covers the rubber ring in Fig. 2.18). Its presence in the medium might have influenced the corrosion process. However, no clear positive or negative correlation was found between the nickel and silicon content of cells with similar immersion times.

It is concluded that nickel was the main element released, and that the release rates of chromium and iron were small and could not be accurately determined. In the following it is assumed that only nickel was released during the corrosion of the alloys.

The potentiostatic deaeration method
After immersion $E_{corr}$ decreased at first, reached a minimum between 10 and 1000 s, and then rose, linearly with log $t$ (Figs 2.22 and 2.23) in the cases of FOR, W77, NP2 and RES, but decreased again after about 10 000 s in the cases of CER and W77. The resemblance between the curves of the FOR, RES, CER and W88 runs is good, the curves of the CER runs overlap. The curves of the W77 and NP2 runs resemble each other less well. The value of $E_{corr}$ increased with the molybdenum content, FOR and W88 showing the highest, CER and W77 the lowest values.

$E_{corr}$ vs $t$ curves of NiCr alloys in artificial saliva (pH 3.65-4 37°C) during the first 12 hours [Meyer77,79], or 24 hours [Hodge77] have been published previously. In these studies $E_{corr}$ increased with the immersion time in the case of high molybdenum content but decreased for alloys with low molybdenum content. The alloy Gemini II (2.0% Mo) showed an initial increase of $E_{corr}$ followed by a decrease, just as for CER and W77 in Figs 2.22-23.

It was expected at the start of the study that $E_{corr}$ would stabilize after some time. Figs 2.22 and 2.23 show that a constant value was not reached after one week. A continuing increase of $E_{corr}$ may cause it to reach the breakdown potential [Hodge77, Hoar66]. Assuming that the breakdown potentials of all NiCrMo alloys are equal, the chance of reaching the breakdown potential is largest for the least corroding alloys, as they have the highest $E_{corr}$ values. Because of this possibility the behavior of $E_{corr}$ at larger immersion time warrants more study.

The duplicates of the measured currents showed good mutual agreement for NP2, RES, FOR, and CER, but not for W77 and W88 (Figs 2.27-32): in the case of W77 the currents differ a factor 10. These differences are attributed to the specimen peculiarity mentioned in the previous section.
Comparison of the results of the two methods.

Figs 2.27-32 show corrosion currents calculated from the values given in Table 2.2, using equations (2-8), (2-9), (2-10), (2-11), and (2-12), and the corrosion currents determined by the potentiostatic deaeration method. The currents determined by the two methods agree well, especially in their time dependency.

The current obtained from the mass loss curve carries more weight, as curve fitting has averaged out the specimen peculiarity. Fig. 2.33 presents all mass loss currents in a single plot. The alloys with the highest molybdenum content show the lowest corrosion rate. This had already been deduced from polarization resistance measurements [Meyer79]. This corrosion inhibiting effect of molybdenum in the alloy can be related to the capacity of molydate to act as an anodic corrosion inhibitor [Vukas86]. The corrosion currents in Fig. 2.33 are very low, namely smaller than 200 nA/cm² [Fonta83,p.345,379].

It follows from the small values of the coefficients of c and d in Table 2.2 that the time dependency of $i_{corr}$ can be described as $h^{b-1}$. This results in a range for the exponent of h of -0.62 to -0.85. The corrosion current consequently decreased almost inversely proportional with time; this is also commonly found for the current in potentiostatic experiments on passivating alloys [Kirch87].
Comparison with results of potentiodynamic studies.

Several potentiodynamic studies of dental Ni-Cr-Mo alloys have been published [Geis-85,87ab, Meyer77,79, Weber80, Mann84, Brück84, Lenz85, Luber86, Wiegm87, Häusl87, Mezge89]. Table 2.6 lists corrosion current values calculated by the polarization resistance method in some of these studies [Lenz85, Wiegm87, Mezge89]. Most of these values are larger than the values found in the present study, only [Wiegm87] finds a similar value. Comparing values is difficult, as the experimental conditions such as medium composition and temperature are different for each study. In none of these studies is an accordance demonstrated between the corrosion current obtained from the polarization resistance method and a corrosion current calculated from mass loss.

**TABLE 2.6**

**CORROSION CURRENTS OF DENTAL Ni-Cr-Mo ALLOYS OBTAINED BY MEANS OF THE POLARIZATION RESISTANCE METHOD.**

<table>
<thead>
<tr>
<th>Alloy (including Ni, Cr and Mo content)</th>
<th>Medium</th>
<th>Corrosion Current [nA/cm²]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceréal (77Ni15Cr3,5Mo)</td>
<td></td>
<td>200</td>
<td>[Lubes86]</td>
</tr>
<tr>
<td></td>
<td>modified Fusayama artificial saliva</td>
<td>2270</td>
<td></td>
</tr>
<tr>
<td></td>
<td>lactic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.05 M</td>
<td>12350</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5 M</td>
<td>920</td>
<td></td>
</tr>
<tr>
<td></td>
<td>acetic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.05 M</td>
<td>196</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5 M</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>propionic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.05 M</td>
<td>196</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5 M</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Micro-Bond N/P² (67Ni22Cr7Mo)</td>
<td></td>
<td>1.2</td>
<td>[Wiegm87]</td>
</tr>
<tr>
<td></td>
<td>modified Fusayama artificial saliva</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wiron 77 (66Ni22Cr9Mo)</td>
<td></td>
<td>1130</td>
<td>[Merge89]</td>
</tr>
<tr>
<td></td>
<td>0.9 % NaCl</td>
<td>modified Fusayama artificial saliva</td>
<td>240</td>
</tr>
<tr>
<td>Micro-Bond N/P² (66Ni13Cr7Mo)</td>
<td></td>
<td>430</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.9 % NaCl</td>
<td>modified Fusayama artificial saliva</td>
<td>430</td>
</tr>
<tr>
<td>Unibond Forte (64Ni12Cr9Mo)</td>
<td></td>
<td>140</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.9 % NaCl</td>
<td>modified Fusayama artificial saliva</td>
<td>120</td>
</tr>
<tr>
<td>Talladium (72Ni14Cr9Mo)</td>
<td></td>
<td>2330</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.9 % NaCl</td>
<td>modified Fusayama artificial saliva</td>
<td>370</td>
</tr>
<tr>
<td>Wiron 88 (60Ni25Cr10Mo)</td>
<td></td>
<td>560</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.9 % NaCl</td>
<td>modified Fusayama artificial saliva</td>
<td>50</td>
</tr>
</tbody>
</table>

Linear relation between $E_{corr}$ and $\log{i_{corr}}$

In Fig. 2.34 $E_{corr}$ and $i_{corr}$ of all the potentiostatic experiments have been plotted on an $E$ vs $\log{i}$ plot. A linear relation is apparent. Regression analysis by the GraphPAD program resulted in a correlation coefficient of -0.9336. The best linear fit satisfies the equation:

$$E_{corr} \text{ [mV NHE]} = -124 \log (i_{corr} \text{ [nA/cm²]}) + 102$$  \hspace{1cm} (2.16)

Figs 2.35 and 2.36 show trajectories of the runs on an $E_{corr}$ vs $\log(i_{corr})$ plot. Trajectories of duplicate runs are only shown when the two runs resulted in different $E_{corr}$ vs $t$ or $i_{corr}$ vs $t$ behaviour, i.e. for FOR, W77 and W88; in these cases the two trajectories still lie near the regression line.
The trajectories of the alloys on a log($i_{cor}$) vs $E_{cor}$ plot therefore resemble straight lines, which is a novel result. It resembles the linear relation found between the log($i_{cor}$) and $E_{cor}$ values of distinct alloys in earlier studies [Schwe63], the difference being the disregard of time dependency in these studies. The linear relation can be explained by assuming that the cathodic current is a function of the potential only, equal for all NiCrMo alloys. The $E_{cor}$ vs $i_{cor}$ line then equals the polarization curve of the cathodic current, the factor of 124 mV/decade in equation (2-16) is Tafel constant. This value is expected for a reaction in which electron transfer is rate limiting [Hoare68]. The actual position on the line would follow from its intersection with the anodic curve, assumed to be distinct for each alloy. The leftward movement along the line is then explained by an anodic current curve that decreases, i.e. shifts to the left, as the passivation layer grows. The anodic current would be controlled by the passive layer, the cathodic current by activation by the electrode potential. Differences between the results of duplicate runs can be explained by differing anodic currents; this variability can be related to the origin of specimen variation.

The validity of the linear relation in other media would allow reinterpretation of determined $E_{cor}$ values. For instance, $E_{cor}$ increased with the molybdenum content of NiCrMo alloys [Hodge77], which can be reinterpreted as a decrease of $i_{cor}$ with molybdenum content, just as was found in this study and in [Geis-88]. The relation could also be used to estimate in vivo corrosion rates from in vitro determined $E_{cor}$ values, for which an improved measuring method has been proposed [Mulle89b].
Determination of the corrosion rates of six dental NiCrMo alloys in an artificial saliva by chemical analysis of the medium using ICP-AES

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Abstract

In order to establish the influence of salivary components upon the corrosion rate of six dental NiCrMo alloys, their mass loss was determined in a medium consisting of a modified Fusayama's artificial saliva to which 300 mg KSCN /L had been added (pH 5.0). Nickel was the main element released; its loss vs immersion time curves on a log-log plot resembled straight lines. The total nickel losses after one week ranged from 0.4 to 12.5 µg/cm². From the nickel loss corrosion currents were calculated. The corrosion currents at 24 hours immersion were up to 67% larger than the currents in a previous study of these alloys, where the medium consisted of a 20 mM KCl-5 mM phosphate buffer solution (pH 7). The alloys with the least molybdenum content showed the largest corrosion current increase.

Nickel is a well known allergen [Counc85]. Biological effects of metallic nickel can be attributed to its corrosion products. For this reason the corrosion rates of nickel alloys used in dentistry are of interest. In a previous study [Mulle90a] we measured the corrosion rates of six dental NiCrMo alloys by the electrochemical potentiostatic deaeration method and by trace metal analysis with Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) of the medium of corrosion test cells. In these experiments the medium consisted of a 20 mM KCl-5 mM phosphate buffer (pH 7) at 37°C. Compared with saliva this medium might be relatively inert because of the lower chloride content, the higher pH, and the absence of thiocyanate. Thiocyanate might stimulate corrosion, since it increases the anodic current in potentiodynamic scanning experiments [Geis-85]. In order for information to be obtained on the corrosion rate of the considered alloys in a more aggressive artificial saliva, the chemical analysis experiments were repeated in a modified Fusayama's solution to which thiocyanate had been added.

The composition of the alloys is given in Table 2.7. The abbreviations CER, W77, NP2, FOR, RES and W88, refer to Ceramalloy II, Wiron 77, Micro-Bond NP2, Forte, Resistal P, and Wiron 88.

Table 2.7. Trademark and composition (%) of the investigated NiCrMo alloys arranged according to increased Mo-content.

Table 2.8. Composition of the medium.

Table 2.9. Concentrations of medium components in the previous and present study (mM).

X indicates an uncertain percentage of accompanying elements, the content of which is generally smaller than 2 %.
Materials and Methods

Fig. 2.37 depicts the test cell, which contains 5 ml of artificial saliva and 25 ml of air. All alloys were investigated in the as-cast condition. Specimens of the alloys were wet ground to a 600 grit finish, ultrasonically cleaned for 2 minutes in distilled water and degreased by placing them for 2 minutes in acetone and in chloroform.

The composition of the medium employed is given in Tables 2.8 and 2.9 and is based on the modified Fusayama's solution as used by Meyer and Nally (1975) and Meyer (1977). Sodium sulphide was not added because it is easily oxidized [Chana84]. The KSCN concentration, viz. 300 mg/L, equals the concentration in the potentiodynamic scanning experiments of Geis-Gerstorfer et al. (1985). Table 2.9 also gives the composition of the medium in the previous study.

Immersion times were 1, 3 and 8 hours and 1, 3 and 7 days. During immersion the test cells were kept at 37°C. For each alloy - immersion time combination three cells were prepared, resulting in a total of 108 cells. Ten cells showed signs of leakage after immersion; they were not further analyzed.

Table 2.10. ICP-AES detection and corresponding specimen mass loss detection limits.

<table>
<thead>
<tr>
<th>Element</th>
<th>ICP-AES Concentration Detection Limit [ppb]</th>
<th>Specimen Mass loss Detection Limit [ng/cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>4</td>
<td>15</td>
</tr>
<tr>
<td>Cr</td>
<td>5</td>
<td>19</td>
</tr>
<tr>
<td>Fe</td>
<td>4</td>
<td>15</td>
</tr>
<tr>
<td>Ga</td>
<td>40</td>
<td>151</td>
</tr>
<tr>
<td>Mo</td>
<td>30</td>
<td>113</td>
</tr>
<tr>
<td>Nb</td>
<td>20</td>
<td>75</td>
</tr>
<tr>
<td>Ni</td>
<td>6</td>
<td>23</td>
</tr>
<tr>
<td>Si</td>
<td>10</td>
<td>38</td>
</tr>
</tbody>
</table>

9) For a medium volume of 5 ml, medium weight 5,000 g, corroding surface area 1,327 cm².

Detailed descriptions of the ICP-AES analytical method have been presented earlier [Mulle89a,90a]; Table 2.10 lists ICP-AES detection limits. Concentrations of Ni, Cr, Mo, B, Si and Fe were determined in all cells. The NP2, FOR and RES cells subject to the longest immersion time were analyzed for the presence of Nb and, in the case of NP2, for the presence of Ga.

The results show that the release of elements other than nickel can be disregarded. The nickel loss \( m \) (in ng/cm²) was calculated from

\[
m = \frac{v c}{S} \]  

(2-17),

where \( v \) is the mass of the medium (5.00 g), \( c \) the measured nickel concentration (ppb) and \( S \) the surface area of the specimen (1,327 cm²). The mass loss data were fitted by the GraphPAD program (ISI Software, Philadelphia, PA, USA) to the equation

\[
\log m = \alpha + \beta u + \gamma u^2 
\]

(2-18),

where \( u = \log h \) and \( h \) (hours) is the immersion time. For each alloy the nickel loss vs the immersion time was plotted on a double logarithmic plot. The fitting curve and its equation are presented, the fitting curve found in the previous study is presented as well. The two curves, obtained in the presence and absence of KSCN, were compared.

It can be derived from the previous study that the corrosion current \( i_{\text{corr}} \) is the following function of the fitting-curve parameters:

\[
i_{\text{corr}} = \frac{z F}{A} \frac{dm}{dt} = \frac{2 z m}{A b 3600} \left( b + 2 \alpha u \right) 
\]

(2-19),

where \( z \) is the valence of nickel (2), \( A \) its atomic weight (58.70), \( t \) the time in seconds, and \( F \) the Faraday constant (96,500 C/Mol). Corrosion currents calculated with this formula were plotted as a function of time, and the calculated corrosion currents at 24 hours immersion were tabulated.
Results

(i) Nickel was detected in all 98 cells. Fig. 2.38 depicts the cumulative nickel loss as a function of immersion time for NP2. The mass loss seems to be a curvilinear function of time. A trend is easily discerned although wide scattering is apparent.

![Fig. 2.38. Nickel loss vs immersion time for Micro-Bond N/P².](image)

Figs 2.39-44 show on double logarithmic plots for each alloy the calculated nickel loss vs the immersion time, and the fitting curves of the previous and the present study. Nickel concentrations measured after one week immersion ranged from 120 ppb (W88) to 3330 ppb (CER).

One of the 98 measured nickel values, viz. 30 ppb for FOR after 9 hours immersion, was excluded from the calculations because it was anomalously low.

The fitting curves of all the considered alloys are combined in Fig. 2.45. The nickel loss is highest for CER and W77, somewhat smaller for NP2 and lowest for W88, FOR and RES, of which the fitting curves almost overlap.

(ii) Varying amounts of silicon were detected in all cells. The largest value found was 13 ppm.

(iii) Boron was detected in 70 cells. The largest value found was 1.0 ppm.

(iv) Iron was detected in 26 cells. Thirteen of these cells were NP2 cells; the average concentration in these cells was 10 ppb.

For Si, B, and Fe no unambiguous relation between the concentration and the immersion time was found.

(v) Chromium was detected in 8 cells. The highest value found was 23 ppb (CER; one week immersion).

(vi) Molybdenum was not detected in any of the cells.

(vii) After one week immersion no niobium was detected in cells of NP2, FOR and RES and no gallium in NP2 cells. Other cells of these alloys were not further analyzed for these elements.

In Fig. 2.46 the corrosion currents of all alloys, calculated from the mass loss, are plotted vs time. Table 2.11 lists the corrosion currents at 24 hours after immersion.

![Fig. 2.39. Nickel loss vs immersion time for Ceramalloy II.](image)

![Fig. 2.40. Nickel loss vs immersion time for Wiron 77.](image)

![Fig. 2.41. Nickel loss vs immersion time for Micro-Bond N/P².](image)
FIG. 2.42. Nickel loss vs immersion time for Restatal.

FIG. 2.43. Nickel loss vs immersion time for Forte.

FIG. 2.44. Nickel loss vs immersion time for Wiron 88.

FIG. 2.45. Fitting curves of nickel loss of all alloys combined.

FIG. 2.46. Corrosion currents, calculated from nickel loss, of all alloys vs immersion time.

TABLE 2.11. Corrosion currents at 24 hours immersion, calculated from the mass losses measured in the previous study (without thiocyanate) and the present study (with thiocyanate).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Current without Thiocyanate [nA/cm²]</th>
<th>Current with Thiocyanate [nA/cm²]</th>
<th>Current Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramalloy II</td>
<td>17.12</td>
<td>27.54</td>
<td>61 %</td>
</tr>
<tr>
<td>Wiron 77</td>
<td>15.32</td>
<td>19.75</td>
<td>29 %</td>
</tr>
<tr>
<td>Micro-Bond N/P²</td>
<td>5.75</td>
<td>9.59</td>
<td>67 %</td>
</tr>
<tr>
<td>Forte</td>
<td>2.72</td>
<td>3.13</td>
<td>15 %</td>
</tr>
<tr>
<td>Wiron 88</td>
<td>2.57</td>
<td>2.60</td>
<td>1 %</td>
</tr>
<tr>
<td>Resistal</td>
<td>2.56</td>
<td>2.85</td>
<td>11 %</td>
</tr>
</tbody>
</table>
Discussion

Just as in the previous study the silicon found is attributed to dissolved silicon grease. Its presence might have interfered with the corrosion process, but no clear positive or negative correlation was found between the nickel and silicon content of cells with equal immersion times. Because of the absence of a relation between the boron concentration and the immersion time, the presence of boron is attributed to contamination, not to corrosion.

It is assumed that the release of chromium and iron can be neglected, and it is concluded that nickel is the main element released by the corrosion process.

In Fig. 2.38 scattering of the mass losses is evident, e.g. one of the determined mass loss values after one week immersion is twice as large as the other two values. On log m vs log t plots (Figs. 2.30-35) the mass loss-immersion time relation is linear. The nickel loss averages after one week of immersion range from 0.50 µg/cm² (W88, RES, FOR) to 4.3 µg/cm² (CER); these values are similar to the previously found values of nickel loss by dental NiCrMo alloys [Mulle89b]. Several other results of the present study are similar to those previously found, viz. wide scattering of the obtained mass losses, almost linear log m vs log t plots, higher corrosion rates for the alloys that contain little molybdenum, corrosion rates that decrease with time, and the same sequence of the alloys when arranged according to corrosion rate; W88, FOR, RES < NP2 < W77 < CER (Figs. 2.35-36). A minor difference is that in the previous study the corrosion rate of CER, in contrast to the other alloys, increased after 24 hours, whereas in the present study the corrosion rate of CER decreased steadily. Figs. 2.39-44 show that the fitting curves lie above the curves of the previous study; consequently the nickel loss is larger.

It follows from the nickel loss that the oxygen depletion of air in the cell is negligible: a specimen area of 1.3 cm² after a loss of 10 µg Ni/cm² has consumed 0.1 µmol oxygen, while in the cell (air volume: 25 ml) 0.25 mmol oxygen is present.

The corrosion currents at 24 hours immersion (Table 2.11) are larger than those found in the previous study. The increase is in particular large for CER and Forte, Resistal, Micro Bond NP2, Wiron 77, Ceramalloy II. The slight difference with the mass losses determined previously in a 20 mM KCl-5 mM phosphate buffer suggests that the corrosion rate is rather insensitive to the presence of thiocyanate, the chloride concentration and the pH at physiological concentrations.

Alloys with the highest molybdenum content show the best corrosion resistance and are also the least sensitive to thiocyanate.

Table 2.12 lists anodic currents values at 600 mV of some dental NiCrMo alloys in absence and presence of 300 mg KSCN/L. The ratio of the two currents can approach 30 000; at potentials below 600 mV this ratio decreases rapidly. Just as in the present study, the effect of thiocyanate was largest for those alloys with the least molybdenum content. Compared to the large ratio values in Table 2.12, the effect of thiocyanate found in this study is small. For this observation two explanations can be given:

(1) The corrosion rate may be controlled by the anodic as well as by the cathodic process. An increase of the anodic current generally results in a smaller increase of the corrosion current [Evans60, p.875]. If the cathodic current controls the corrosion rate, then an increase of the anodic current (i.e. a shift to the right in an Evans plot) will result in only a small increase in the corrosion current.

(2) The effect of thiocyanate on the anodic current depends on the potential, and may be low at the actual corrosion potential.

Conclusions

The elemental mass loss of corroding NiCrMo alloys during the first week after immersion in artificial saliva was determined. The corrosion currents calculated from the measured mass loss are very small and decrease with immersion time. The sequence of the alloys according to increasing corrosion rate is Wiron 88, Unitek Forte, Resistal, Micro Bond NP2, Wiron 77, Ceramalloy II. The slight difference with the mass losses determined previously in a 20 mM KCl-5 mM phosphate buffer suggests that the corrosion rate is rather insensitive to the presence of thiocyanate, the chloride concentration and the pH at physiological concentrations.

Alloys with the highest molybdenum content show the best corrosion resistance and are also the least sensitive to thiocyanate.

Acknowledgements

We thank Hans Balke for performing the ICP-AES analysis, and Jeanne Kruchowski for proofreading.
2-5 Determinations of mass loss of other alloys

This section describes the application of mass loss determination by ICP-AES to Xerxes (another NiCrMo alloy), Vitallium (a CoCr alloy), and some noble alloys; the mass loss of Micro-Bond N/P in a medium consisting of 0.1 M lactic acid plus 0.1 M NaCl was also determined.

Specimen preparation, the corrosion test cell, the method for chemical analysis of the medium and the data analysis method were identical to those described in the second article.

The mediums were identical to those described in the articles, except in the study where the medium contained lactic acid. The 20 mM KCl-5 mM phosphate medium of the first and second article is hereafter called 'the pH 7 buffer'; the medium of the third article, a modified Fusayama's solution to which 300 mg KSCN/L has been added but in which sulphide is absent, is similarly called 'the pH 5 artificial saliva'.

The following studies were mainly done for illustrative purposes, to show that the developed methods can be more widely applied, and are for this reason not extensively discussed.

2-5.1 Xerxes

Introduction
Mass loss by Xerxes 220 (abbreviated as 'Xerxes'), a dental NiCrMo alloy, in the pH 5 artificial saliva was determined.

Table 2.13 gives the composition of Xerxes. The alloy is manufactured by Elephant Edeldental B.V. (Hoorn, The Netherlands).

<table>
<thead>
<tr>
<th>Element</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>66</td>
</tr>
<tr>
<td>Chromium</td>
<td>22</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>8.5</td>
</tr>
<tr>
<td>Niobium + Tantalum</td>
<td>3.6</td>
</tr>
<tr>
<td>Titain</td>
<td>0.25</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.2</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Results
Eight cells were prepared. After immersion nickel, boron and silicon were determined in the medium. Fig. 2.47 gives the nickel loss vs the immersion time. Fig. 2.48 gives the corrosion current calculated from this mass loss together with the currents calculated for other NiCrMo alloys shown in the third article. The corrosion current could not be calculated for an immersion time shorter than five hours, as the slope of the mass loss fitting curve for that time is negative (Fig. 2.47).

Discussion
The negative slope of the mass loss fitting curve for short immersion times in Fig. 2.47 is attributed to a chance effect of scattering of mass losses. For larger immersion times, the corrosion current of Xerxes behaves the same as other NiCrMo alloys with similar molybdenum content (Fig. 2.48).
2-5.2 Vitallium

**Introduction**

The composition of Vitallium is given in Table 2.14. The alloy is commonly used for implants and for removable partial dentures [Steinb82, Siebe89]. Mass loss was determined in the pH 5 artificial saliva.

**TABLE 2.14. COMPOSITION OF VITALLIUM [Forsc86].**

<table>
<thead>
<tr>
<th>Element</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt</td>
<td>60.6</td>
</tr>
<tr>
<td>Chromium</td>
<td>31.5</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>6.0</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.75</td>
</tr>
<tr>
<td>Manganese</td>
<td>&lt;2</td>
</tr>
</tbody>
</table>

**Methods**

Table 2.15 gives the detection limits of elements analyzed.

**TABLE 2.15. ICP-AES DETECTION LIMITS AND CORRESPONDING MASS LOSS DETECTION LIMITS.**

<table>
<thead>
<tr>
<th>Element</th>
<th>ICP-AES concentration detection limit [ppb]</th>
<th>Specimen mass loss detection limit [ng/cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt</td>
<td>6</td>
<td>23</td>
</tr>
<tr>
<td>Chromium</td>
<td>15</td>
<td>57</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>12</td>
<td>45</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.6</td>
<td>2.3</td>
</tr>
<tr>
<td>Iron</td>
<td>3</td>
<td>11</td>
</tr>
</tbody>
</table>

* For a medium weight of 5.00 g and a corroding surface area of 1.527 cm².

**Results**

Eighteen cells were prepared. After immersion, cobalt was detected in all cells. In three cells chromium was detected (3 d immersion: 13 ppb, 7 d: 13 and 16 ppb), in six cells manganese (3 and 7 d immersion: 2 - 7 ppb). No iron or molybdenum was detected. Fig. 2.49 gives the mass loss and the mass loss fitting curve vs time; Fig. 2.50 gives the corrosion current vs time as calculated from the mass loss fitting curve. For comparison, similar curves of three NiCrMo alloys, shown in the third article, are given as well.

**Discussion**

Fig. 2.50 shows that the corrosion current of Vitallium behaves similarly as Wiron 88.

In *vivo* the corrosion current of CoCr alloys may also decrease: *in vivo* there is no correlation between corrosion product concentration and implantation duration [Miche87], suggesting that most material is released directly after implantation. Moreover, serum levels of cobalt, nickel and chromium decrease during the first 30 days after implantation of a CoCr alloy (F-75 alloy: about 65% Co, 27-30% Cr) [Koege84].

**Fig. 2.49. Mass loss of Vitallium vs immersion time.**

**Fig. 2.50. Corrosion currents of Vitallium and three NiCrMo alloys vs immersion time.**

- Vitallium
- Wiron 88
- Micro-Bond MPF
- Ceramall II
2.5.3 Noble alloys

Introduction

In a pilot study the mass loss of a pure gold, two gold alloys (Bermudian Y and Orion WX), two PdAg alloys (Orion Argus and Splendor) and a PdCu alloy (Orion Vesta) were determined. The investigated alloys were pure gold, two gold alloys (Bermudian Y and Orion WX), two PdAg alloys (Orion Argus and Splendor) and a PdCu alloy (Orion Vesta). The composition of the alloys is given in Table 2.17. All alloys were manufactured by Elephant Edelmetall BV (Hoorn, The Netherlands).

Materials and methods

Specimens were cut by Elephant Edelmetall. The ICP-AES analysis was performed at the chemical laboratory of Elephant Edelmetall. Elements analyzed, concentration detection limits and corresponding specimen mass loss detection limits are given in Table 2.16. Table 2.16 gives limits of the IC/AES facility of Elephant Edelmetall.

Table 2.16: Limits of the ICP/AES facility of Elephant Edelmetall.

<table>
<thead>
<tr>
<th>Element</th>
<th>Limit (ppb)</th>
<th>Limit (ng/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag, Cu, Zn, Fe</td>
<td>2-8</td>
<td>5-10</td>
</tr>
<tr>
<td>Au, Re</td>
<td>5-19</td>
<td>19-38</td>
</tr>
<tr>
<td>Sn, Ga, Rh, Pt, Pd, Ag, Cu, Zn, Fe</td>
<td>2-8</td>
<td>5-10</td>
</tr>
</tbody>
</table>

Results

In a pilot study the mass loss of a pure gold, two gold alloys (Bermudian Y and Orion WX), two PdAg alloys (Orion Argus and Splendor) and a PdCu alloy (Orion Vesta) were determined. The investigated alloys were pure gold, two gold alloys (Bermudian Y and Orion WX), two PdAg alloys (Orion Argus and Splendor) and a PdCu alloy (Orion Vesta). The composition of the alloys is given in Table 2.17. All alloys were manufactured by Elephant Edelmetall BV (Hoorn, The Netherlands).

Table 2.17: Determined mass losses of noble alloys in μg/cm².

<table>
<thead>
<tr>
<th>Gold alloys</th>
<th>Palladium-silver alloys</th>
<th>Palladium-copper alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Gold 100Au</td>
<td>Bermudian Y (86Au12Pd2In)</td>
<td>Orion WX (52Au38Pd5In2Ga)</td>
</tr>
<tr>
<td>immersion time</td>
<td>3d</td>
<td>7d</td>
</tr>
<tr>
<td>in pH 7 buffer</td>
<td>-</td>
<td>*ND</td>
</tr>
<tr>
<td>-</td>
<td>*ND</td>
<td>*Nd</td>
</tr>
<tr>
<td>in pH 5 artificial saliva</td>
<td>-</td>
<td>*Nd</td>
</tr>
<tr>
<td>-</td>
<td>*Nd</td>
<td>*Nd</td>
</tr>
</tbody>
</table>

*ND* indicates "Nothing Detected"

* indicates results of the next test cell.
Discussion
The results show that the corrosion test method consisting of mass loss by chemical analysis of the medium can also be applied to noble alloys.

In Table 2.17 the mass loss of pure gold is very low. Only in the pH 5 artificial saliva could some mass loss be detected - it was less than 0.1 µg/cm² after one week. The reported rhenium loss by Orion WX is assumed to be erroneous, as the alloy does not contain rhenium in appreciable quantities (J.M. Van der Zel, personal communication). If this interpretation is correct, then the two gold alloys, Bermudent Y and Orion WX, have similar very low mass losses. The rhodium released by Bermudent Y is added in small amounts (<2%) to the alloy as a grain refiner and hardener (J.M. Van der Zel, personal communication).

The PdAg alloys show a somewhat larger elemental release. In the pH 7 buffer no mass loss by Orion Argos is detectable, in the pH 5 artificial saliva the alloy shows losses of about 0.24 µg Pd/cm² and 0.30 µg Ag/cm². Splendor shows losses of about 0.1 µg/cm² in both mediums.

The PdCu alloy, Orion Vesta, shows palladium loss in all, and copper loss in almost all determinations. In the pH 7 buffer these losses were smaller than 0.1 µg/cm²; in the pH 5 artificial saliva they were about 1.0 µg Pd/cm² and 0.15 µg Cu/cm². This alloy shows the largest losses of all six alloys.

The corrosion current can roughly be estimated by comparison of the mass loss with the mass loss of dental NiCrMo alloys after one week, assuming that the time dependency of the corrosion current is similar to that of NiCrMo alloys. The third article mentions values of about 0.45 µg/cm² for mass loss of the least corroding NiCrMo alloys; the PdAg alloys show mass losses that are a bit lower, the PdCu alloy about twice this value. It would follow that the corrosion currents of palladium alloys match the corrosion currents of the best NiCrMo alloys.

The corrosion current of the best dental NiCrMo alloys after 1.5 h immersion, about 0.02 nA/cm², has the same magnitude as the values given by Merger for palladium alloys, values obtained by the polarization resistance method [Mezer89,p.150-152]. For Orion WX the value was 20 to 40 nA/cm², with the immersion time ranging from 1 to 2 hours (P.M. Merger, personal communication).

2.5.4 Micro-Bond N/P² in 0.1 M lactic acid + 0.1 M NaCl

Introduction
Mass loss of Micro-Bond N/P² in a 0.1 M lactic acid + 0.1 M NaCl medium (pH 2,3) was determined. The composition of Micro-Bond N/P² is given in Table 2.1.

Methods
The medium was obtained by mixing appropriate amounts of lactic acid, sodium chloride and water. Correlation between elemental mass loss and immersion time was determined by the GraphPAD program, assuming a linear relation. From the linearity between mass loss and immersion time, for each component j, a corrosion current \( i_{corr} \) is calculated:

\[
i_{corr} [\mu A/cm^2] = \frac{F}{z_j r_j} \sum \frac{m}{A_j}
\]

where \( z_j \) is the valence of the element released (assumed values [Bard85]: 2, 3, 6, 2 and 4 for Ni, Ga, Cr, Mo, Fe and Si), \( r_j \) its release rate, \( A_j \) its atomic weight; \( F \) is Faraday's constant.

Results
Fifteen cells were prepared. In the cells nickel, gallium, chromium, molybdenum, iron, boron and silicon were detected. Figs 2.50-56 give the mass loss vs immersion time. For the first five elements a linear relation of mass loss vs time was observed (Table 2.18) and the associated fitting curves are given in the figures.

Table 2.18. Elemental release rates calculated from the mass loss data, ratios of these elemental release rates and the nickel release rate, and the ratios of the elemental weight percentages in the alloy and the nickel weight percentage.

<table>
<thead>
<tr>
<th>Element</th>
<th>Release rate</th>
<th>Element release rate / nickel release rate</th>
<th>Element wt% / nickel wt% in the alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>1.244</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.121</td>
<td>0.097</td>
<td>0.204</td>
</tr>
<tr>
<td>Gallium</td>
<td>0.361</td>
<td>0.291</td>
<td>0.131</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>0.076</td>
<td>0.061</td>
<td>0.106</td>
</tr>
<tr>
<td>Iron</td>
<td>0.065</td>
<td>0.052</td>
<td>0.075</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.071</td>
<td>0.057</td>
<td>0.011</td>
</tr>
<tr>
<td>Boron</td>
<td>0.0053</td>
<td>0.0043</td>
<td>-</td>
</tr>
</tbody>
</table>

The corrosion current calculated from the release rates in Table 2.18, using Eq. (2-20), equals 2.3 µA/cm², with no contribution of boron taken into account. The contribution of silicon to the current is 0.27 µA/cm² and is suspect, as the silicon in the medium is partly attributed to the dissolving of the silicon grease used.
FIG. 2.51. Nickel loss of Micro-Bond NIP vs time in 0.1 M lactic acid + 0.1 M NaCl.

FIG. 2.52. Chromium loss of Micro-Bond NIP vs time in 0.1 M lactic acid + 0.1 M NaCl.

FIG. 2.53. Gallium loss of Micro-Bond NIP vs time in 0.1 M lactic acid + 0.1 M NaCl.

FIG. 2.54. Molybdenum loss of Micro-Bond NIP vs time in 0.1 M lactic acid + 0.1 M NaCl.

FIG. 2.55. Iron loss of Micro-Bond NIP vs time in 0.1 M lactic acid + 0.1 M NaCl.

FIG. 2.56. Silicon loss of Micro-Bond NIP vs time in 0.1 M lactic acid + 0.1 M NaCl.
Nickel and gallium are the main elements released (Fig. 2.58). Table 2.16 shows that the dissolving process during corrosion cannot be imagined as a simple scraping off of a surface layer, but that instead some elements (Ni, Ga) dissolve faster than one might expect from the composition of the alloy, while others (Cr, Mo, Fe) dissolve slower.

In the first and second article a medium with few salivary components was used because added oxidizable salivary components might, by reacting with oxygen, deplete the oxygen inside the cell during the long immersion time, which in turn might end anodic current inhibition. In this study the total amount of lactic acid in the medium is 0.5 mmol, the total amount of oxygen in the air of the cell 0.25 mmol (third article). One lactic acid molecule can react with three molecules of oxygen, hence reaction with lactic acid could remove all oxygen, a process that microorganisms can accelerate strongly. The corrosion rate in Table 2.16 is larger than the rates in the articles, which can be explained by the much lower pH, and by the occurrence of the above mentioned effect of oxygen depletion.

A previous study [Geis-87a], where the same medium was used but where aeration was constant, yielded lower values for the mass loss of Micro-Bond N/P², which can be explained by the absence of an oxygen depletion effect. Four dental NiCr alloys were investigated. After one week the nickel loss was about 7.5 and 4 µg/cm² for Micro-Bond N/P² and Wiron 88, and 3800 and 4100 µg/cm² for Euro-Ceram (a NiCr alloy without molybdenum) and Ultratek (a NiCr alloy containing beryllium) [Geis-87a,Figs 7-8]. Anodic protection [Fonta83,p.210] could however also be the cause of the lowered metal loss, as the specimens were squeezed in the specimen holder by means of platinum wires and were possibly in electrical contact with these wires.

Obviously more research is needed to determine the stability of dental NiCrMo alloys with respect to mediums of low pH and low oxygen concentration.
2-6 Commentary

Section 2-6 gives additional comment to the obtained results. Similar results of other researchers are given. Some aspects of the clinical significance are discussed, and subjects for further research indicated.

2-6.1 The methods

The articles present the first electrochemical determination of the corrosion rate of a passive alloy as a function of time. The articles are consequently of general interest. Because of their slow alteration during corrosion, the slowly corroding NiCrMo alloys are suitable model systems for corrosion research. The study of strongly corroding systems, on the contrary, is complicated because of their rapid evolution: dissolved corrosion products may act as additional oxidizers, corrosion products may precipitate upon the metal surface, and holes and crevices may arise.

The two measurement methods, the potentiostatic deaeration method and chemical analysis of the medium, are complementary. The first method yields the corrosion potential and current, allowing the determination of the $E_{corr}$ vs $i_{corr}$ relation. The method is involved, as one needs a special test cell, gas bottles, a potentiostat, an ADDA converter, a microcomputer and a heat bath. The method is also time-consuming, as it takes one week to measure one specimen. Performing many experiments is tedious, which makes it difficult to determine the average corrosion behavior. The method demands continuous attention, especially during deaeration. The other method, chemical analysis of the medium, yields the elements that go into solution. Only a $37^\circ$C oven is needed. Many test cells are easily handled simultaneously, permitting the quick determination of the average corrosion behavior and its dispersion. An ICP-AES facility must be available. During immersion the cells must be watched for leakage, but this is only a minor nuisance.

The potentiostatic deaeration method measures the cathodic current, which in turn is equal to the sum of the corrosion currents due to all types of corrosion that can occur: in addition to uniform corrosion, crevice corrosion, pit corrosion, intergranular corrosion, stress corrosion and wear corrosion. As a consequence one can, provided the corrosion due to all other corrosion types can be neglected, measure by this method the corrosion current due to each of these corrosion types.

The use of silicon grease minimizes the chance of crevice corrosion occurring in the crevice between the specimen and the specimen holder.

2-6.2 Mass loss determinations

A decreasing mass loss rate is commonly observed in mass loss experiments of dental alloys, such as for amalgam [Brune81,84d] and noble alloys [Mober85].

The articles show that NiCrMo alloys mainly release nickel; this is also found for NiCrFe alloys [Miche87].

The second and third articles confirm the previously reported large variation in corrosion resistance of individual NiCr alloys [Weber83].

Scattering of corrosion rates

Large scattering of the corrosion rate also occurs for CoCr alloys in vitro [Brune84b], for CoCr implants in vivo [Miche87] and for amalgam in vitro [Brune81,84a, Mober85,a,b,c,88] and in vivo [Enwon87].

While testing alloys one should be aware that the clinically important property may be not the average behavior but instead be behavior deviant from the average, in particular the incidence of large transgressions.

The wide scattering in mass loss of individual alloys under identical experimental conditions can be explained by a variable intensity of wear corrosion or of crevice corrosion. It follows from the second article that the anodic process is probably sensitive to wear corrosion, but the cathodic process is not, as the anodic process is influenced by the thickness of the passive layer, but the cathodic process is not.
2.6.3 The time dependency of the corrosion potential

In Figs 2.22-23 the corrosion potential decreased directly after immersion, reached a minimum after between 10 and 1000 s and then rose linearly with log \( t \). This behavior can be explained by assuming that during submersion the specimen first assumes the 'Billiter-potential' [Verte61 p.87], which for many metals has the value of 479 mV, and that metal oxides in a high-oxidation state, formed at the air/metal interface before immersion, oxidize the metal next, causing its potential to drop. The latter process is assumed to level off after 10 to 1000 s.

The increasing corrosion potential after 10 to 1000 s might be attributed to a depletion of base components from the corroding metal surface [Kaes79, p.151]. Increasing corrosion potentials are however also found for pure metals where such an ennoblement is impossible, e.g. for pure silver and palladium [Ishiz69] (Fig.2.59). Here the increase can only be explained by a thickening of the passive layer that diminishes the anodic current more strongly than it diminishes the cathodic current. A similarly increasing corrosion potential has been found for gold alloys during the first 24 hours after immersion [Brugi73] (Fig.2.60).

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Linear \( E_{cor} \) vs log \( t \) curves similar to those in the second article have been found for titanium [Abdel81] (Fig.2.61).

The second article asserts that a rising corrosion potential could eventually reach the breakdown potential, which is often a pitting potential (\( E_{pit} \)). In a recent study of the pitting potential of NiCrMo alloys in a 0.1 M NaCl, this potential was 730 mV at pH 7, independent of the molybdenum content [Geis-89, Fig.2] (Fig.2.62). At lower pH, the pitting potential was lower than 730 mV for alloys with a molybdenum content lower than 6 %, and was higher for alloys with a higher molybdenum content. One can estimate the time, here called the 'induction time', \( t_{ind} \), to reach the pitting potential.

From Fig. 2-23 it follows that the corrosion potential of Unitek Forte increased during the first run linearly with log \( t \) according to

\[
E_{cor}(t) = -464 + 122 \log t
\]

for \( t > 10^4 \) s. Section 2.7.2 shows that such a linear increase with log \( t \) can be derived mathematically. It follows from extrapolation that the pitting potential of 730 mV shall be reached after a \( t_{ind} \) of

\[
10^4 \times 730 = 1 / 112 \times 6.12 \times 10^9 \text{ s,}
\]

i.e. 194 year. The chance of such an event occurring in vivo seems remote.
At lower pH the induction time may be shorter, especially for alloys with a lower molybdenum content. The $E_{\text{cor}}(t)$ curve of Micro-Bond N/P2 (7 % Mo) during the first 12 h after immersion in a modified Fusayama solution, pH 5, has been given [Meyer77,Fig.8] (Fig.2.63). Assuming a linear increase with log $t$, it follows from the $E_{\text{cor}}$ values at 6 and 12 h, that $E_{\text{cor}}(t)$ can be approximated as:

$$E_{\text{cor}}(t) = -284 + 110 \log t.$$
A linear decreasing log $i_{pot}$ vs log $t$ has been found for nickel in 1 M $H_3PO_4$, 1 M $NaH_2PO_4$, 1 M $Na_2HPO_4$ and 1 M $Na_3PO_4$ [Maier84] (Fig. 2.64). The coefficient of log $t$ is often, but not always, close to -1. At lower pH the current decay rate is generally less, in some cases the current remains constant. In one case a late current increase similar to the late increase of Ceramalloy is found (Fig. 2.64c).

A linear decreasing log $i_{pot}$ vs log $t$ has also been found for nickel in a borate buffer (pH 8.3) [Flis85] (Fig. 2.65). NiP alloys, on the contrary, show linearly increasing curves on these plots.

For amalgam a monotonously decreasing potentiostatic current that approaches zero has been found [Marek80] (Fig. 2.66).

**FIG. 2.64** Linear log $i_{pot}$ vs log (time) curves of nickel in phosphate solutions at several pH [Maier84]. The original figures have been modified by the author: curves recorded at higher temperatures have been removed.

**FIG. 2.65** Linear log $i_{pot}$ vs log (time) curves of nickel and NiP alloys in a borate buffer (a), in a borate buffer with chloride (b), and in a borate buffer with sulphate (c). [Flis85, Figs 4, 7, 9].

**FIG. 2.66.** Potentiostatic current decay of several amalgams in 1 % NaCl: Tytin (A), Artstaloy (B), Disperosalloy (E) and Velvalloy (L) [Marek80].
For scratches upon 304L stainless steel at pH 0, 4.7 and 14, and upon bismuth at pH 14, a linear decreasing log ipot vs log t has been found, also with a coefficient of log t close to -1 [Burst83ab,84, Misra84] (Figs 2.67-70).

The \( t^n \) time dependency for the corrosion current found in the articles for NiCrMo alloys and in section 2.5.2 for Vitallium was also found for the \( ipot \) of creviced samples of surgical CoCr alloys. At higher potentials deviations occurred similar to the late increase found for Ceramalloy in the second article (Figs 2.71).
It is concluded from Figs 2.65-71 that the time dependency of the corrosion current of NiCrMo alloys and of Vitallium resembles the time dependency of the potentiostatic current of several other passive alloys.

Prepassivation or anodizing
The decreasing corrosion current suggests the use of precorrosion in order to lower the corrosion rates of metallic restorations. In this context it is of interest that no inflammation occurred after the second implantation of NiCrMo alloys that had caused inflammation after the first implantation [Henst80], and that precorrosion of a AgPdCu alloy lowered its cytoxicity [Niemi85]. These results suggest that biological effects of implanted metals can be avoided by corroding the metal before implantation, i.e. by 'anodizing' it, covering it with an artificially thick passive layer. Anodizing is a standard method for protecting aluminum against corrosion; it specifically prevents pit corrosion [White85]. Prepassivation has also been proposed as a means of avoiding the metallic taste that patients often experience directly after placement of restorations [Laute85]. Prepassivation would particularly make sense when the metal is resistant to wear corrosion, or, when not resistant, is not subject to it, because otherwise the applied layer would be worn away.

In vivo the potential range of three to nine month old NiCr restorations is 120 - 210 mV [Gubsk74] (cited by [Brück84]). From Eq. (2-16) a corresponding corrosion current range of 0.13 - 0.72 nA/cm² is calculated. In vivo potentials have also been measured of specimens of dental metals cemented to the facial surfaces of teeth of baboons [Geril80]. After one week the potential of Micro-Bond N/P2 specimens was 30 mV, the potential of Howmedica III (Ni32Cr44Mo9Si2Sn) specimens 71 mV. Application of Eq. (2-16) then yields 3.8 and 1.8 nA/cm² for the associated corrosion currents. In both studies the potentials consequently suggest that in vivo corrosion currents are very low. Equation (2-16) may however be inappropriate for metals placed in the oral cavity, one reason being that the salivary oxygen concentration is lower than in the medium of the second article, which can lower as well as enhance the corrosion rate. The applicability of equations similar to Eq. (2-16) in the oral cavity warrants further investigation, as an established validity would allow the determination of the in vivo corrosion rate from the easily obtainable in vivo corrosion potential.

Extrapolation of the current in Eq. (2-16) to 810 mV (the equilibrium potential of the oxygen/water redox couple at pH 7), yields the exchange current density of the cathodic current. From the linearity follows a value of 10⁻⁵.71 nA/cm². When a NiCrMo alloy is electrically connected to a second metal with a larger exchange current density of the cathodic current, an enhanced anodic current of the alloy, i.e. galvanic corrosion, can be expected.

If the explanation of the Ecorr - log (icorr) linearity by Tafel behavior of the cathodic current is correct, then the corrosion current that can be calculated with this relation from a measured corrosion potential represents the sum of all types of corrosion currents that might be present in addition to uniform corrosion: crevice corrosion, pit corrosion, intergranular corrosion, stress corrosion and wear corrosion. Just as for the potentiostatic desaturation method (see section 2-6.1) one could determine the corrosion current due to each of these corrosion types when all other corrosion types can be neglected.
As mentioned in section 1-2, the role of oxygen in passivation is still controversial [Bockr70, p.1324]. It has been claimed that passivation is caused by inhibition of the anodic current by oxygen [Uhlgl79], but the opinion that an oxide layer causes passivation [Evans71] appears to be more popular. The first article confirms the existence of an influence of oxygen upon the anodic current during passivation. The decrease of the anodic current with immersion time is on the other hand more easily explained by hindrance of the anodic current by a thickening oxide layer. It is concluded that both anodic current inhibition by oxygen, and barracading by an oxide layer, contribute to the passivation of dental NiCrMo alloys. Such combined action during passivation has been proposed previously [Andre64].

The secondary rise, as described in the first article, makes it difficult to determine the magnitude of the primary rise accurately. The secondary rise could be suppressed by the addition of a small amount of oxygen to the nitrogen purging gas. Such an amount should suffice for inhibition of the anodic current but should result in an insignificant cathodic current.

The oxygen concentration threshold for inhibition of the anodic current should be determined, and should be compared with the very low oxygen concentration in saliva and plaque4. Fig. 2.10 shows that the threshold for Micro-Bond N/P2 lies below a partial oxygen pressure of 0.10 %, the lower the threshold of an alloy, the higher its in vivo corrosion resistance may be.

As long as these thresholds are unknown, patients should be advised to brush their restorations well. This removes anaerobic plaque that might enhance corrosion by oxygen depletion. The advice should be given particularly to patients who suffer from complaints attributed to metallic restorations. Such a corrosion inhibiting effect of brushing can also explain the observation that tarnish of restorations is less in patients with a better oral hygiene [Mege89, p.125].

4 Inhaled air contains 21 % oxygen, exhaled air 16 % oxygen. The PO2 on the anterior tongue is 16.4 %, on the posterior surface of the tongue 12.3 % [Eskow71]. Oxygen exchange between air and saliva is slow, except possibly in mouth breathers [Globe79]. The PO2 of saliva leaving the salivary glands varies between 5.6 and 16.0 %, after secretion, bacterial respiration causes the PO2 of saliva to drop quickly. On the floor of the mouth the range is from nil to 0.4 % [Globe79], and in the maxillary and mandibular buccal folds 0.3 to 0.4 % [Eskow71]. The oral microflora is predominantly anaerobic. The increased presence of obligate anaerobic bacteria [Birz77] as plaque ages indicates a very low PO2. Strict anaerobes, which in vitro only grow when PO2 < 0.5 %, are found in periodontal pockets, on the surface of sub-gingival plaque near gingival tissue, deep in dental paule, and in necrotic dental pulps. As fresh plaque matures, anaerobiosis increases [Morri79].
2-7 The relation between polarization resistance and corrosion current during passivation

2-7.1 The Stern-Geary equation

The Stern-Geary equation \([Stern57]\), for our purposes written as

\[ i_{\text{cor}} = \frac{R_{\text{pol}}}{2.303 / \beta_a + 2.303 / \beta_c} \]  

(2-21)

calculates the corrosion current \(i_{\text{cor}}\) from the polarization resistance \(R_{\text{pol}}\) and the Tafel constants \(\beta_a\) and \(\beta_c\) of the anodic and cathodic currents.

As the conditions under which the equation is valid are of interest in the rest of section 2-7, its derivation is given here. The equation is derived under the assumption that both the anodic and cathodic currents can be described by the Tafel equation:

\[ V = a \pm \beta \log i \]  

(2-22)

It follows that one can write for the anodic current \((i_{\text{an}})\) and the cathodic current \((i_{\text{cath}})\):

\[ V = \frac{i_{\text{an}}}{\beta_a} \]  

(2-23)

\[ V = \frac{i_{\text{cath}}}{\beta_c} \]  

(2-24)

At the corrosion potential the two currents are equal:

\[ i_{\text{an}}(E_{\text{cor}}) = i_{\text{cath}}(E_{\text{cor}}) \]  

(2-25)

During a potentiodynamic scan the potential \(V\) is varied, using an external power source, and the net externally applied 'potentiodynamic current', \(i_{\text{pod}}\), measured. The current equals:

\[ i_{\text{pod}}(R_{\text{pol}}) = i_{\text{an}}(R_{\text{pol}}) = i_{\text{cor}} \]  

(2-26)

At the corrosion potential \(i_{\text{pod}} = 0\).

During a potentiodynamic scan:

\[ i_{\text{pod}} = \frac{i_{\text{an}}}{\beta_a} - \frac{i_{\text{cath}}}{\beta_c} \]  

(2-27)

The polarization resistance \(R_{\text{pol}}\) is defined by

\[ \left( \frac{dV}{\text{d}E_{\text{cor}}} \right) = \frac{i_{\text{cor}}}{R_{\text{pol}}} \]  

(2-28)

After differentiating and substituting \(V = E_{\text{cor}}\) one obtains:

\[ \frac{\text{d}i_{\text{pod}}}{\text{d}V} = 2.303 \left( \frac{E_{\text{cor}} / \beta_a}{\beta_a} + \frac{i_{\text{cor}} / \beta_c}{\beta_c} \right) \]

\[ = 2.303 \left( \frac{i_{\text{cor}}}{\beta_a} + \frac{i_{\text{cor}}}{\beta_c} \right) \]

Hence:

\[ i_{\text{cor}} = \frac{2.303 R_{\text{pol}}}{(1/\beta_a + 1/\beta_c)} \]

the Stern-Geary equation.
2.7.2 An equation for passive alloys similar to the Stern-Geary equation

The second article yielded idealizations for the anodic and cathodic current of NiCrMo alloys. From these idealizations, an equation similar to the Stern-Geary equation can be derived. General validity of this derived equation would explain the apparent validity of the Stern-Geary equation during passivation. For the derivation of such an equation, the anodic and cathodic current during passivation have to be expressed as a function of electrode potential and/or time.

It is assumed that the anodic current of passivating alloys equals the potentiostatic current of these alloys; the anodic current is assumed to depend only upon the time, being described by the equation:

\[ i_{an} = i_{an}(t) = i_{ao} \cdot t^{-\alpha} \]  

(2-28)

where \( t \) is the immersion time, and \( \alpha \) is approximately 1 [Kirch87]. The corrosion current \( i_{cor} \) is then obviously also described by Eq. (2-28):

\[ i_{cor} = i_{cor}(t) = \frac{V}{\beta_c} \]

(2-29)

The second article shows that the cathodic current can be idealized by Tafel's law, Eq. (2-23):

\[ i_{ca}(V) = i_{ca} \cdot 10 \]

with the Tafel constant having the value of 120 mV. How common such Tafel behavior is remains to be demonstrated; it can be tested by checking whether during a potentiodynamic scan the cathodic branch is independent of the scanning rate and immersion time.

It follows from Eqs (2-23) and (2-28), that at the corrosion potential \( E_{cor} \):

\[ V = E_{cor}(t) = \frac{\beta_c \log (i_{ca}/i_{ao}) + \alpha \beta_c \log t}{s} \]

(2-30)

Thus a linear rise of corrosion potential with \( \log t \) is derived, in accordance with Figs 2-11, 2-22 and 2-23, and with a study of the corrosion potential of titanium [AbdEl81]. From a typical \( \beta_c \) value of 120 mV and an \( \alpha \) value of 1, a tenfold increase in immersion time would result in an \( E_{cor} \) increase of 120 mV.

During a potentiodynamic scan the applied potential \( V \) is a function of time:

\[ V = V_0 + s (t - t_0) \]

(2-31)

where \( t_0 \) is the starting time of the scan, \( V_0 \) is the potential at \( t_0 \), and \( s \) the scan rate. It follows that:

\[ V = V_0 + s t \]

(2-32)

and it follows from Eqs (2-23), (2-26), (2-28), and (2-32) that:

\[ i_{ca}(V) = \frac{i_{ao} \cdot (t_0 + (V_0 - V)/s)}{10} \]

(2-33)

Obviously, \( i_{ca}(E_{cor}) = 0 \), and

\[ i_{ca}(t) = (E_{cor}) = i_{cor} \]

(2-34)

Substituting Eq. (2-33) in Eq. (2-27), using Eq. (2-34), and substituting \( V = E_{cor} \), yields:

\[ R_{pol} = \frac{1}{\frac{1}{R_{pol}} + \frac{1}{2.303 / \beta_c - \alpha / s \cdot t}} \]

(2-35)

the sought equation. Equation (2-35) is similar to the Stern-Geary equation, the difference being the replacement of the term 2.303 / \( \beta_c \) by the term - \( \alpha / s \cdot t \).

If the product \( s \cdot t \) becomes large, Eq. (2-35) reduces to an equation proposed [Praza68] for a modified Stern-Geary equation in which the 2.303 / \( \beta_c \) term has been neglected:

\[ i_{cor} = \frac{R_{pol}}{R_{pol} \cdot 2.303 / \beta_c - \alpha / s \cdot t} \]

(2-36)

with \( K \) equal to \( \beta_c / 2.303 = 52 \) mV, assuming a value of 120 mV for the Tafel constant. This calculated value of \( K \) agrees well with the reported range of 51 - 105 mV [Callo76]. Note that \( i_{cor} \) in Eq. (2-36) still depends on time, as \( R_{pol} \) is time-dependent.

From a value of 120 for \( \beta_c \), a value of 0.019 is calculated for the first term between brackets in the denominator of Eq. (2-35). For the second term between brackets, assuming values of 1 for \( \alpha \), 0.01 mV/s for \( s \), and 3600 s for \( t \), a value of 0.028 is obtained. The expression between brackets in Eq. (2-35) then becomes negative, and \( R_{pol} \) must then be negative as well. In that case Equation (2-36) obviously is inadequate, and results are suspect that were obtained by applying Eq. (2-36) to data from experiments in which the scanning rate was low and the immersion time short. Correction is simple, if one can be certain that application of Eq. (2-35) is allowed.

For the polarization resistance method the advantage has often been claimed that it tests the corrosion resistance of an alloy in a short time [Geis-87b]. The foregoing shows that at short immersion times in particular, the corrosion current calculated with the Stern-Geary equation may differ greatly from the actual corrosion current.

It was asserted at the beginning of this chapter that for passivating metals the polarization resistance method is invalid. Next, another method was developed for measuring corrosion rates, and it was just stated that the polarization resistance method may sometimes be applied to passivating alloys after all. Have I come full circle? The answer is 'No', as one can only state in hindsight that the application of the polarization resistance method is valid. One must first have at one's disposal reliable data on the anodic and cathodic current, data that can only be obtained by means of the potentiostatic desorption method.

Good results of the application of the Stern-Geary equation may originate from the validity of an equation resembling the Stern-Geary equation. Such an equation may be valid providing battery behavior of the passivating oxide layer is insignificant. This battery behavior is discussed in the following section.
2.7.3 Battery behavior

The first article mentions that the cation current between the metal and the oxide layer ("anodic current") can differ from the cation current by metallic ions between the oxide layer and the medium ("anodic dissolution current"). The difference has been called the "film formation current" (Fig. 2.74), and these currents have been discussed in models for the time dependency of the potentiostatic current during the potentiostatic dissolving of iron [Kirch87]. At pH 1 both anodic currents decrease almost linearly on a log i vs log t plot until 1000 s (Fig. 2.75). Thereafter the thickness of the passive layer becomes constant and the film formation current becomes zero, the anodic current equaling the anodic dissolution current. At pH 8.4, however, the anodic dissolution current is zero during the entire immersion. All anodic current goes into film formation; the anodic current continues to decrease linearly on a log i vs log t plot after 1000 s (Fig. 2.75). Similarly in austenitic 304 L stainless steel, most of the anodic current after scrubbing at high pH goes into the build-up of the oxide layer, and does not go into anodic dissolution [Burst83a].

![Diagram of battery behavior](image)

**FIG. 2.74.** The anodic current of ions entering the oxide layer can differ from the anodic dissolution current, the current associated with metal ions entering the medium. The difference is the film formation current.

![Graph of battery behavior](image)

**FIG. 2.75.** An anodic current can be present in the absence of an anodic dissolution current (the latter current is here denoted as 'corrosion current', i_corr) [Kirch87, Fig. 7-8].

An oxide layer that can 'absorb' an anodic cation current in the absence of an anodic dissolving cation current, can function as a battery when the charge 'stored' in the oxide layer can be released again later. More generally, battery behavior of the oxide layer can also be associated with the occurrence of reversible reactions such as:

$$\text{MO}_2 + 2 \text{H}^+ + 2 e^- \rightarrow \text{MO} + \text{H}_2\text{O}$$

The oxidation state of metal oxides in oxide layers can indeed be a non-integral variable [Vette62, Attun86]. At high potential the reaction goes to the left, at low potential to the right: after connection of the metal to an external high potential power source the metal oxide layer stores electrical energy which it releases when the external potential falls. During storage the current is anodic, during release cathodic, giving hysteresis of the current during a cyclic potential scan.

Presumably the oxide layer upon every passive metal can, to a certain extent, store and release charge in this manner during a cyclic potentiodynamic scan. The associated anodic and cathodic currents are unrelated to metal dissolving and oxygen reduction reactions.

![Graph of battery behavior](image)

**FIG. 2.76.** Cyclic polarization curve for a small battery current.

Assume firstly that the currents caused by such battery behavior are small compared to the anodic dissolution current and the cathodic oxygen reduction current (Fig. 2.76). Battery behavior then leads to the addition of an extra term to Eq. (2-26) called the 'battery current', \(i_{\text{bat}}\). Then:

$$i_{\text{pod}} = i_{\text{an}} - i_{\text{bat}}$$

Let the battery current be proportional to the scanning rate and not depend on the voltage and the time. Let the proportionality factor be \(b\). Then:

$$i_{\text{bat}} = b \cdot s$$

and

$$\frac{d}{dV} i_{\text{bat}} = 0;$$

which causes Eq. (2-33) to remain valid. However, \(i_{\text{pod}}\) is not zero at \(E_{\text{cor}}\) any more, but is \(i_{\text{an}}\) larger during forward scanning. \(E_{\text{cor}}\) lies approximately \(E_{\text{cor}} + R_{\text{cor}} q_{\text{cor}}\) above the potential at which \(i_{\text{pod}}\) is zero: one must then take care to determine the polarization resistance at the corrosion potential and not at the potential of zero applied current. As the battery current increases, this potential difference also increases.

Secondly, let the battery current be large in comparison to the anodic dissolving current and the cathodic oxygen reduction current (Figs 2.77-78). This
then causes strong hysteresis of the applied current during a cyclic potentiodynamic scan, as the battery current is positive during the rise of the applied potential and negative during its fall. Such strong hysteresis of the potentiodynamic current is indeed commonly found during cyclic potentiodynamic scans of dental amalgams, dental gold and AgPd alloys, and orthodontic wire alloys [Nomot77, Wrig81, Sarka79abc,82,83, Johns83, Nadal85, Mezge89] (Figs 2.79-85: in some of these figures the current is plotted vs the potential)\(^5\). The cathodic current during the hysteresis is often implicitly attributed to the reduction of an oxidator in the medium, but reduction of the oxide layer is more plausible\(^6\). Battery behavior is suggested by the applied current often having the same magnitude but opposite sign during the forward and reverse scan. Moreover, a tenfold increase or decrease in scanning rate during potentiodynamic scans causes a similar increase and decrease of the applied current [Sarka79c:discussion, Geis-87b] (Fig.2-86), hence a fixed amount of charge appears to be necessary to effect a certain voltage change, which also suggests an oxide layer charging / discharging mechanism.

\(^5\) Some of the curves given by Mezger show an anodic current during the reverse scan that lies to the right of the anodic current during the forward scan. This can be attributed to pit corrosion during the reverse scan initiated at high potential.

\(^6\) Sarkar (1983) remarked that hysteresis indicates changes in the alloy surface due to passive film growth.
FIG. 2.83. Cyclic polarization curves of $81.5\,\text{Pd}_{15}\text{Sn}_{5.5}\,\text{Ga}$ in two artificial salivas [Nadal85, Figs 13-14].

a. Permachrome

b. Elgiloy

c. Experimental titanium alloy

d. Nitinol

FIG. 2.84. Cyclic polarization curves of Permachrome (a stainless steel), Elgiloy (a CoCr alloy), an experimental titanium alloy, and Nitinol (a NiTi alloy) [Sarka83].

a. Unibond Forte

b. Wiron 88

c. Talladium

d. Micro-Bond N/²

e. Trindium

f. Titanium

FIG. 2.85. Cyclic polarization curves of several dental alloys in 0.9 % NaCl [Mezge89]. For Micro-Bond N/² and Talladium the anodic current was initially larger at the start of the reverse scan compared to the forward scan. This is attributed to pit corrosion.
FIG. 2.86 Scanning rate dependence of the polarization curve of NiCr alloys [Geis-87b].

Alloy A: without molybdenum (72Ni, 3Cr, 2Si, 1Fe, 1Mn)
Alloy B: with 10% molybdenum (61Ni, 25Cr, 9Mo, 1Fe, 1Mn).

Thus battery behavior can be detected by performing cyclic polarization scans. In the absence of battery behavior the currents during the forward and backward scan will have identical sign and magnitude. A decreasing anodic current may also cause hysteresis during a cyclic voltage scan, mimicking battery behavior. One can check for a decreasing anodic current by performing three-way scans: forward, backward, and forward again. Battery behavior will cause the currents during the two forward scans to be equal, but time dependency shall cause the current during the second forward scan to be lower. Scanning-rate dependence of the polarization curve can also be used to detect battery behavior.

Obviously the Stern-Geary equation and Eq. (2-35) are not applicable for describing the corrosion current of passive metals that show strong battery behavior, such as the alloys of which the polarization curves are given in Figs 2.79-85.

Battery behavior cannot interfere in the potentiostatic deaeration method, as this method does not involve potential scanning, nor can non-Tafel behavior of the anodic and cathodic current interfere in this method, as the corrosion current is not calculated from Tafel constants but is instead determined directly.

CHAPTER 3

In vivo electrical potential measurements

3.1 Introduction

In research, agreement of in vivo and in vitro values of a parameter measurable under both conditions helps in alleviating the ever present doubt concerning the applicability of in vitro results. The electrical potential of a restoration, which can be measured in vivo as well as in vitro, is therefore of interest. In addition, it is of interest because of its possible correlation with adverse effects of metallic restorations.

However, the published measurement methods of the in vivo potential were found to have flaws. For this reason an improved measurement method was developed. Two articles have been written on in vivo potential measurement: the first one describes the new method, and the second one discusses its application to the restorations of a group of 28 healthy students.