

Scientific paper

The Effect of pH Value of a Simulated Physiological Solution on the Corrosion Resistance of Orthopaedic Alloys

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Received: 24-08-2011

Abstract

Abstract

Metals and alloys used in orthopaedics and dentistry are exposed *in vivo* to various agents and environmental conditions. One of the important factors that determine the corrosion behaviour of metallic biomaterials is the pH of the environment. The corrosion resistance of stainless steel 316L (Fe/Cr18/Ni10/Mo3), titanium and titanium alloy Ti-6Al-4V (Ti90/Al6/V4) was studied in terms of their electrochemical properties and biodegradation in simulated physiological solutions of different pH values (4.5, 6.5, 7.5 and 8). The electrochemical characteristics of individual metal components were also investigated using cyclic voltammetry, linear polarization and potentiodynamic polarization methods. The concentration of dissolved metal ions released during 32 days immersion under simulated physiological conditions was determined by inductively coupled plasma mass spectroscopy.

The corrosion behaviour of stainless steel 316L is strongly affected by the pH of the physiological solution in the range from 4.5 to 8.0. The corrosion resistance was enhanced at higher pH and the concentrations of released metal ions lower. The behaviour of titanium and its alloy however is almost independent of the pH.

Keywords: Orthopaedic alloys; pH; simulated physiological solution; potentiodynamic measurements; ICP-MS

1. Introduction

Numerous biomaterials are playing an important role in orthopaedic implants used to improve their function, or to replace parts of skeletal body system. The majority of components of orthopaedic implants are manufactured from metallic alloys, the most frequently used being stainless steel AISI 316L, cobalt-chromium alloy Co-28Cr-6Mo, commercially pure titanium (c.p. Ti) and titanium-based alloys like Ti-6Al-4V and Ti-6Al-7Nb. Stainless steel implants are employed as temporary implants to help bone healing, as well as fixed implants like joint replacements. Cobalt and titanium-based materials are used primarily for permanent implants, such as hip and knee replacements and dental prostheses.

Metallic orthopaedic implants have to be biocompatible, corrosion and wear resistant, and durable. The elastic modulus of all metals is higher than that of natural bone, but it is desirable that it is as low as possible. The low elastic modulus of titanium implants, coupled with their lower specific density, is thus more effective than the other two alloys. One of the most important requirements for the metallic materials is high corrosion resistance. Due to the high concentration of chloride ions and elevated temperature (37 °C), body fluids are highly aggressive for metallic implants. These materials can form a protective film on the surface that hinders the corrosion process at the surface and prevents the release of metal ions into surrounding tissue.¹ The composition, structure and properties of the protective layer depend on various factors asso-

ciated with properties of the material itself (i.e., chemical composition, microstructure and surface condition) and of the medium the material is exposed to (i.e., chemical composition, pH and temperature).¹ The pH of the medium is an important factor that could affect the behaviour of the metal. The pH of the gluteus medius control measure point is 7.39 ± 0.05 .² Upon bone fracture, the pH of the fracture region may decrease to value as low as 5.2 and then increase to physiological value within a week.³ The pH of the environment at the implant interface in a patient with a well fixed, but broken, cup was shown to increase to 7.75 along the acetabular base, and to 7.85 in the acetabular cup itself.³ Moreover, the pH of the tissue in septic and aseptic loosening varied between 4.38 and 7.7.² Changes in pH may affect the thermodynamic stability of the metals and alloys, reducing the corrosion resistance of the material. Metals can then generate ions that are released into the surrounding tissue and possibly lead to toxic, carcinogenic, genotoxic, idiosyncratic and allergic effects.^{4–6}

In vitro studies of electrochemical behaviour of orthopaedic alloys are scarce.^{7–9} Vasilescu et al. investigated the effect of the pH of the Ringer physiological solution, at values of 2.5, 6.9 and 8.9, on the behaviour of various Ti-based alloys.⁷ Self-passivation of the Ti-alloys was established over this range, with a broad passive region extending up to high positive potentials (about 4 V). Al-Mayouf et al. studied the behaviour of the Ti-30Cu-10Ag alloy in artificial saliva containing fluoride ions.⁸ The severity of attack by these ions was dependent on both fluoride concentration and the pH. Hodgson et al. studied Ti alloys in simulated body fluid electrolyte solution and in simple saline solutions containing Ca^{2+} and PO_4^{3-} ions at different values of pH (2.0, 4.6 and 7.4).⁹ The decrease in photocurrent intensity at lower pH was attributed to a thinner oxide film formed on Ti and its alloys with decreasing pH, due to reduced stability and increased dissolution of the passive film.

Due to its importance the effect of the pH of the physiological environment on the electrochemical behaviour of orthopaedic alloys and their constituent metal should be studied further. In the present study the electrochemical and corrosion behaviour of stainless steel 316L, titanium and Ti-6Al-4V alloy was investigated in simulated physiological solutions (SPS) in the pH range from 4.5 to 8.0. This pH range is expected to be relevant during the long-term exposure of orthopaedic alloys in human body subjected to various conditions, such as infection, fracture, various diseases, etc. The study was carried out using electrochemical techniques – cyclic voltammetry, linear polarization and anodic potentiodynamic measurements – and biodegradation tests performed using inductively coupled plasma – mass spectroscopy (ICP-MS) for the measurement of metal ion release.

The aim of this study was to investigate the effect of pH on the electrochemical behaviour of stainless steel, titanium and Ti-based alloy and individual metal compo-

nents in simulated physiological solution using electrochemical methods and long-term immersion test.

2. Experimental

2.1. Materials and Solutions

The following materials were used in this study: **stainless steel 316L** (Fe/Cr18/Ni10/Mo3; annealed), **Ti-6Al-4V** alloy (Ti90/Al6/V4; annealed), **titanium** (purity 99.6%, annealed), **nickel** (purity 99.0%), **molybdenum** (purity 99.9%) and **aluminium** (purity 99.0%), all supplied by Goodfellow (Cambridge Ltd., UK); stabilized **iron** (carbon steel, AISI 1045, maximum 0.63 weight % of alloying elements), supplied by Metal Ravne, Slovenia, **chromium** (purity 99.8%) supplied by GFE Metalle und Materialien, GmbH, Nuremberg, Germany, and **vanadium** (purity 99.8%) supplied by A.D. Mackay, Inc. NY, USA.

Materials were purchased in the form of 2 mm thick foil. Samples used for electrochemical measurements were cut from the foil in the shape of discs of 15 mm diameter; those for biodegradation tests were cut in the shape of plates with dimensions 5 cm × 1 cm. All samples were mechanically ground successively with SiC papers of gradations 500, 800, 1000, 2400 and 4000. The samples were cleaned with acetone in an ultrasonic bath for two minutes, double-rinsed with distilled water, and dried in a stream of nitrogen.

Measurements were performed in simulated physiological solution (SPS), so-called Hanks solution, with the composition given in Table 1. The pH of Hanks solution was adjusted to 4.5, 6.5, 7.5 and 8.0 by the addition of HCl or NaOH solutions. All chemicals used for the preparation of solutions were of *p.a.* purity supplied by Kemika (Zagreb, Croatia), and Carlo Erba Reagents (Rodano, Italy).

Table 1. Chemical composition of simulated physiological solution

Compound	Concentration (g/L)
NaCl	8.00
KCl	0.40
$\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$	0.25
NaHCO_3	0.35
$\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$	0.06
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	0.19
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	0.40
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	0.06
glucose	1.00

2.2. Electrochemical Measurements

Electrochemical measurements were performed in a three-electrode corrosion cell (volume 350 mL, Autolab, Ecochemie, Netherlands) at a temperature of 37 ± 0.1 °C. A specimen embedded in a Teflon holder, with an area of

0.785 cm² exposed to the solution, served as the working electrode. A saturated calomel electrode (SCE, 0.2415 V vs. saturated hydrogen electrode, SHE) was used as reference electrode and carbon rods as counter-electrode. Electrochemical experiments were carried out with a Parstat 2263 potentiostat/galvanostat and controlled by Powersuite software.

Prior to measurements, the samples were allowed to stabilize under open circuit conditions. During that time, the open circuit potential, E_{oc} , was measured as a function of time. Depending on the material, the stabilization process took from 1 to 24 h. Longer stabilization times were usually required for titanium and its alloy. The stable, quasi-steady state potential reached at the end of the stabilization period is denoted as the corrosion potential, E_{corr} . Electrochemical measurements were carried out following the stabilization. The linear polarization measurements were performed vs. E_{corr} at a potential range of ± 20 mV, using a 0.166 mV/s potential scan rate. The values of polarization resistance, R_p , were deduced from the slope of the fitted current density vs. potential curves, using Powersuite software. Potentiodynamic measurements were performed using a 1 mV/s potential scan rate, starting at 250 mV negative to E_{corr} . The potential was then increased in the anodic direction until the breakdown potential, E_b , was reached.

For each sample, measurements were performed at least in triplicate. Mean values and standard deviations of R_p were then determined. Representative values of E_{corr} and anodic polarization curves were selected.

Cyclic voltammetry measurements were carried out on non-stabilized samples using a potential scan rate of 20 mV/s. The potential range was determined individually for each material of interest.

2. 3. Measurements of Concentration of Released Metal Ions

Stainless steel 316L and Ti-6Al-4V plates were prepared as described in section 2.1. They were immersed in 100 mL of simulated physiological solution of two pH values, 4.5 and 7.5, contained in sterile plastic tubes. Tubes were placed in a thermostat bath and the temperature maintained at 37 ± 0.1 °C. The immersion test lasted for 32 days. Each experiment was performed in duplicate. Sterile plastic tubes containing only SPS served as blank samples. The experimental conditions were as for the test samples.

In order to follow the biodegradation of alloys, the concentration of dissolved metal ions (Fe, Cr, Ni, Mo, Ti, Al and V) in SPS was measured using inductively coupled plasma – mass spectroscopy (ICP-MS). During the immersion period, 1 mL of solution aliquot was taken from each solution after the following immersion periods: 3, 5, 8, 10, 18, 25 and 32 days. The aliquot was added to a tube containing 1 mL 2% HNO₃ solution and stored for ICP-MS analysis.

Concentrations of dissolved ions were measured using an Agilent 7500ce ICP-MS instrument (Agilent Technologies, Palo Alto, USA) equipped with MicroMist pneumatic nebulizer and a peltier-cooled spray chamber. 1500 W RF power was used. Ar carrier and make-up gas was used at 0.85 and 0.2 L min⁻¹, respectively. Octopole reaction system (ORS) in kinetic energy discrimination mode with 5 mL min⁻¹ of He collision gas was used to reduce the effect of polyatomic interferences from the sample matrix. To further reduce the influence of matrix, a method of standard additions was used for calibration (11 points). Results were expressed as mean concentrations (c_{avg}) in $\mu\text{g L}^{-1}$ of duplicate measurements standard deviation (σ). The concentrations of metal ions measured in blank samples were subtracted from the concentrations measured in test samples. Limit of detection (LOD) was calculated based on the relation $\text{LOD} = c_{avg} + 3\sigma$.

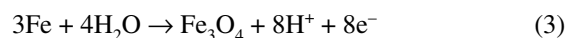
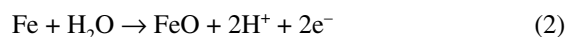
3. Results and Discussion

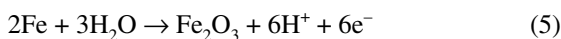
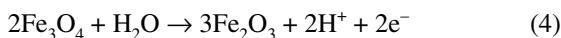
3. 1. Cyclic Voltammetry

Cyclic voltammograms of stainless steel 316L and Ti-6Al-4V alloys, together with the individual metal components (Fe, Cr, Ni, Mo, Ti, Al and V) were recorded in SPS at pH 4.5, 6.5, 7.5 and 8.0 in order to correlate the current-potential characteristics of the alloys to those of the constituent metals.

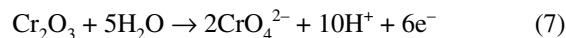
3. 1. 1. Stainless Steel 316L

Cyclic voltammograms were recorded at different pH values for Fe, Cr, Ni and Mo metals (Fig. 1). At pH value 4.5, iron exhibits no tendency to passivation and the current density increases abruptly as soon as the anodic current density is reached, i.e. at -0.7 V (Fig. 1a). This increase is related to the dissolution of iron and formation of Fe(II) species which are released into solution (eq. 1).¹⁰ It is noteworthy that for the purpose of this work only general reactions are presented,¹⁰ without any intention to discuss the mechanism behind each of these reactions. In the reverse cycle a hysteresis loop appeared, indicating that the dissolution continues even after potential reversal. Pitting corrosion occurs at the same time. At higher pH values, iron is oxidized to a solid layer consisting of FeO, Fe₃O₄ and Fe₂O₃, (eqs. 2–5).^{10,11} This process is indicated by the progressive decrease in current density in the anodic range. Since both Fe₃O₄ and Fe₂O₃ have the structure of spinel, Fe₃O₄ can be easily transformed to γ -Fe₂O₃, (eq. 4), or the latter can be formed directly from Fe metal (eq. 5). Therefore, at pH values higher than 6.5, the passivity is established in a broader potential range.





In the presence of air, chromium metal spontaneously forms a layer of chromium(III) oxide (eq. 6).^{10,11}



A cyclic voltammogram for nickel was recorded in the potential range from -1.0 V to 0.4 V (Fig. 1c). In the anodic range the peak A_1 is related to the formation of NiO (eq. 8).^{10,11} At pH 4.5 and 6.5, anodic peak A_1 ap-

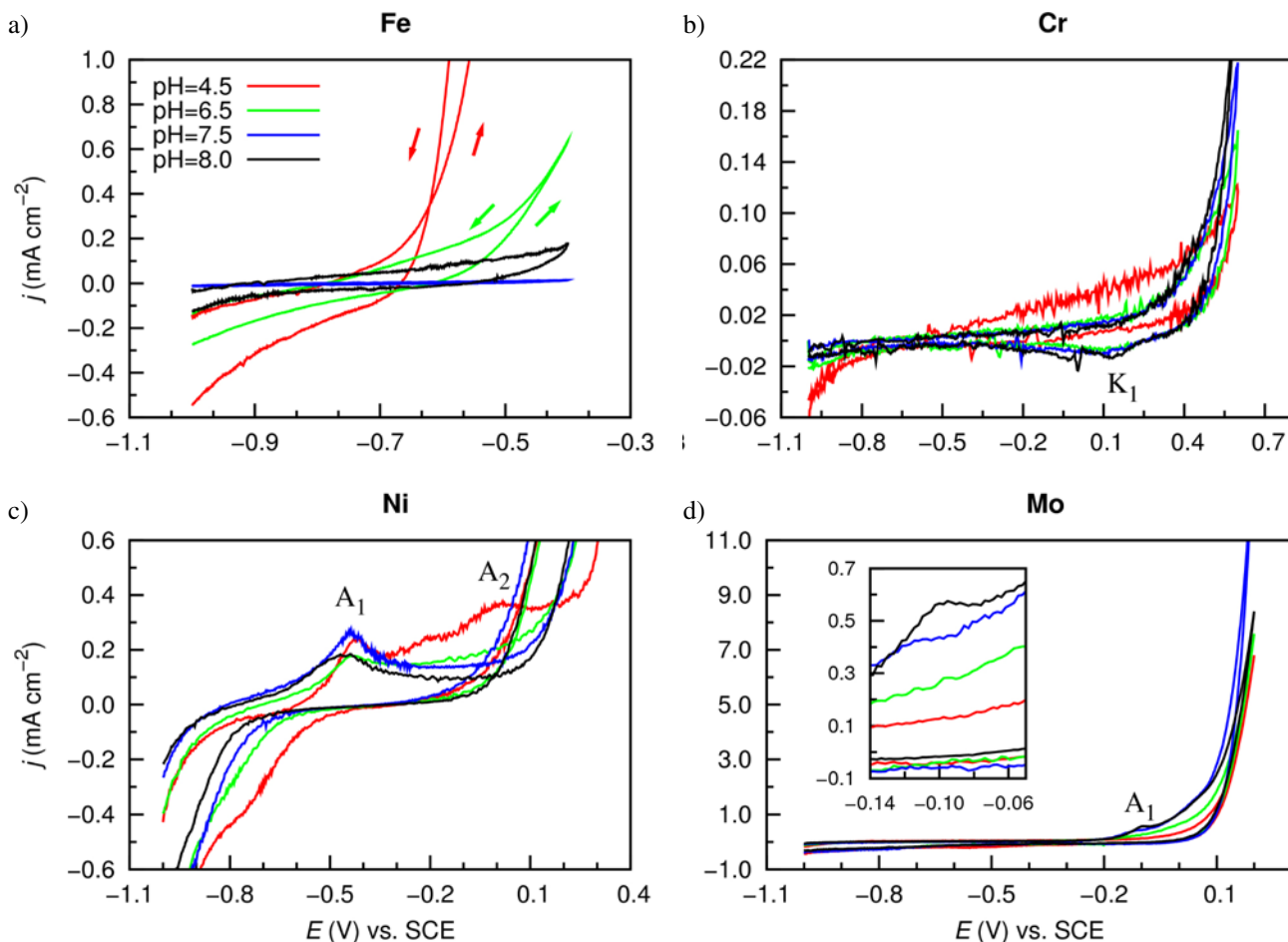
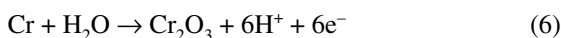
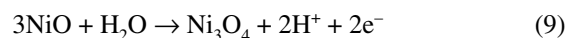
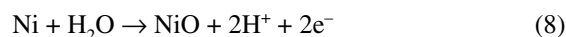


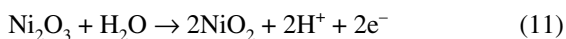
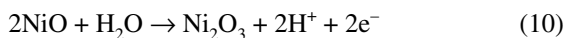
Figure 1. Cyclic voltammograms recorded for (a) iron, (b) chromium, (c) nickel and (d) molybdenum in simulated physiological solution of different pH values (4.5, 6.5, 7.5 and 8.0). $dE/dt = 20$ mV/s.

This layer enables the formation of a broad passive range with low current densities (Fig. 1b) which is protective. In contrast to iron metal, the shape of the voltammograms does not vary significantly with pH. The current density within the passive range is highest at pH 4.5 and decreases slightly at higher pH values; however, the differences are not substantial as they are for iron. At potentials more positive than 0.4 V, an increase of current density limits the passive region and denotes the beginning of the transpassive oxidation of chromium(III) oxide, forming Cr(VI) species (eq. 7). In the reverse scan, at 0.1 V, a small cathodic peak K_1 appears, which is related to the reduction of Cr(VI) to Cr(III) species.

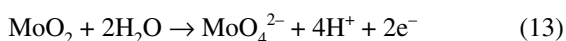


pears at -0.4 V, whereas at higher pH values, it is shifted to the slightly more negative value of -0.5 V. Its height increases slightly with decreasing pH value. The second anodic peak A_2 appears only in a solution of pH 4.5. It is most probably related to the oxidation of Ni(II) oxide to Ni(III) oxide (eqs. 9,10). At more positive potentials, the current density starts to increase abruptly, due to transpassive oxidation to Ni(IV) oxide (eq. 11), and evolution of oxygen. In the reverse cycle, hysteresis of current density occurs accompanied by pitting corrosion.





The cyclic voltammogram for molybdenum was recorded in the potential range from -1.0 V to 0.2 V. Passivity is established spontaneously due to the formation of MoO_2 oxide (eq. 12) which protects the underlying metal up to approximately -0.1 V (Fig. 1d). At more positive potentials the current density starts to increase due to transpassive oxidation of Mo(IV) to Mo(VI) (eq. 13).^{10,11} The potential of transpassive oxidation is more negative for solutions with higher pHs of 7.5 and 8.0.



The behaviour of individual metal components in simulated physiological solution can be summarized by stating that the electrochemical behaviour of chromium provides the highest corrosion protection with the lowest current density and a broad region of passivity. Molybdenum behaves similarly to chromium but with a narrower passivity region. Nickel shows complex behaviour, with the formation of various oxides. All these three metals exhibit the general trend of decreasing current density with increasing pH value, due to the formation of more stable oxide layers at neutral and slightly alkaline solutions. Of all the investigated metal components, iron shows the most pronounced dependence on the pH of the simulated physiological solution with the transition from active dissolution at the lowest pH of 4.5 to passivation at pH 7.5 and 8.0.

Cyclic voltammograms for stainless steel 316L in SPS of different pHs were recorded in the potential range from -1.0 V to 0.2 V and in a broader range from -1.0 V to 0.6 V (Fig. 2). An anodic peak A_{1a} is located at -0.7 V

at pHs 4.5 and 6.5. At pHs 7.5 and 8.0, the anodic feature A_{1b} appears at -0.4 V (Fig. 2a). Under neutral and slightly alkaline conditions the passivation film on stainless steel is composed of iron (outer layer) and chromium oxides (inner layer).^{11–15} The latter oxide is formed spontaneously during exposure to air. Comparison of cyclic voltammograms for stainless steel 316L (Fig. 2) and individual metal components (Fig. 1) leads to conclusion that anodic peaks A_{1a} and A_{1b} refer mainly to the oxidation of iron to iron(II) oxide and then to iron(III) oxide. Nickel and molybdenum may also contribute to the formation of the passive film, namely through the oxidation of nickel to nickel(II) oxide, and molybdenum to molybdenum(IV) oxide.¹³ The passive region extends to about 0.4 V and is followed by a transpassive region and oxygen evolution. The transpassive region comprises the oxidation to higher-valence species and oxides. At more positive potentials the current density starts to increase abruptly and a hysteresis loop is formed (Fig. 2b). The formation of the latter is related to the initiation and progression of pitting corrosion.

The potential at which the current density starts to increase is most negative at pH 4.5. Furthermore, the extent of hysteresis loop is most pronounced at this pH. This result leads to the conclusion that stainless steel 316L is more susceptible to pitting corrosion at lower pH value of simulated physiological solution.

3. 1. 2. Titanium Metal and Ti-6Al-4V Alloy

Cyclic voltammograms for aluminium were recorded in the potential range from -1.4 V and -0.6 V (Fig. 3a). Aluminium does not show any tendency towards passivation and the current density starts to increase abruptly at potentials more positive than -0.6 V. The current density reaches high values and after potential scan reversal it forms a hysteresis loop characteristic of pitting corrosion.

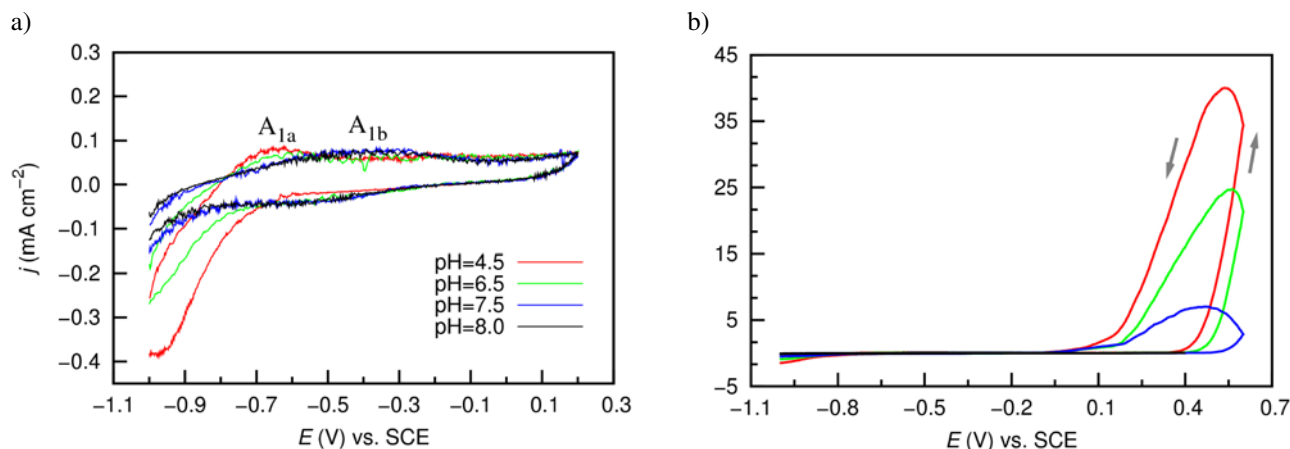


Figure 2. Cyclic voltammograms recorded for stainless steel 316L in simulated physiological solution of different pH values (4.5, 6.5, 7.5 and 8.0) in two potential ranges: (a) from -1.0 V to 0.2 V, and (b) from -1.0 V to 0.6 V. $dE/dt = 20$ mV/s.

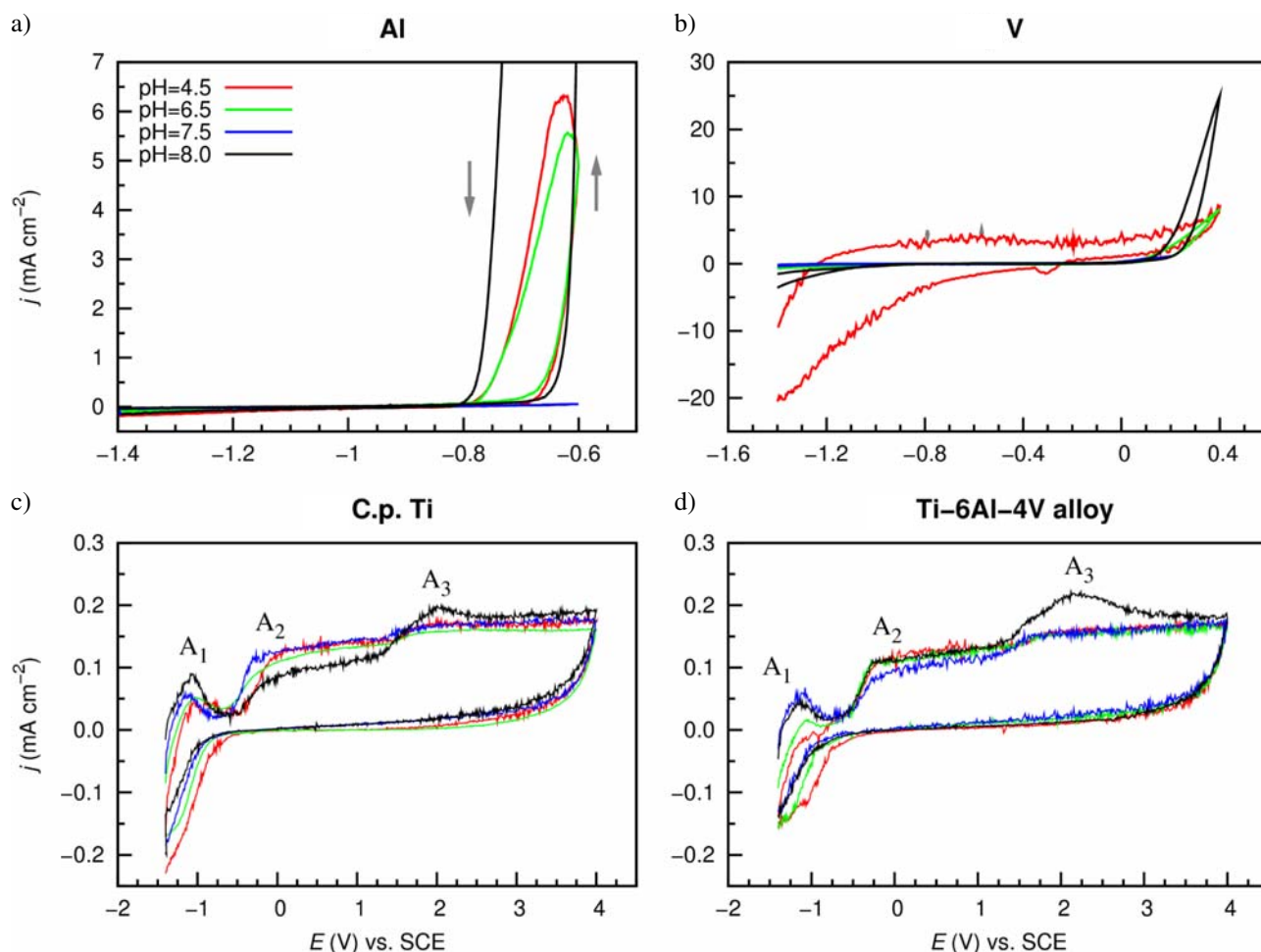
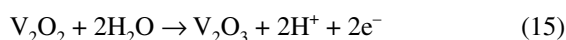


Figure 3. Cyclic voltammograms recorded for (a) aluminium, (b) vanadium, (c) titanium, and (d) Ti-6Al-4V alloy in simulated physiological solution of different pH values (4.5, 6.5, 7.5 and 8.0). $dE/dt = 20$ mV/s.

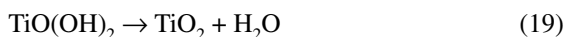
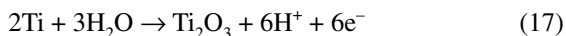
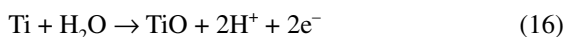
Cyclic voltammograms for vanadium reveal a broader potential range than those for aluminium, extending up to 0.2 V (Fig. 3b). Although vanadium is a valve metal, its oxides do not provide strong corrosion protection to the underlying metal as is the case with other valve metals. The passive range is established up to a potential of 0.2 V due to the formation of V_2O_2 and/or V_2O_3 oxides (eqs. 14,15).^{16,17} V_2O_2 is stable up to approximately -0.3 V, whereas V_2O_3 is stable up to 0.05 V.^{16,17} At more positive potentials the increase in current density is related to the dissolution of V_2O_3 and the formation of soluble species of the type VO_3H^- ,^{16,17} which are formed at pH values between strongly acidic, where VO^{2+} species are formed, and strongly alkaline solutions, where VO_4^{3-} species are formed.



Cyclic voltammograms for titanium were recorded in the potential range from -1.4 V to 4 V (Fig. 3c). An

anodic peak A_1 is observed at -1.0 V that corresponds to the formation of titanium sub-oxides, TiO and Ti_2O_3 (eqs. 16, 17).^{18–20} At higher pH, the current of the anodic peak A_1 increases slightly. At approximately 0 V (at pH values 4.5 and 6.5) and -0.2 V (at pH values 7.5 and 8.0) a second anodic peak A_2 is formed. It corresponds to the formation of titanium(IV) oxide, TiO_2 , which is the most stable titanium oxide (eq. 18).^{18–20} The current density remains almost constant up to 1.5 V. Within this range the oxide layer becomes thicker.^{18,19} The thickening continues up to 9 nm and reaches a maximum at the third anodic peak, A_3 , at approximately 2.0 V. The peak A_3 is more pronounced at pH 7.5 and 8.0. At this potential oxygen evolution occurs, which takes place via electron transfer across the oxide and without transpassive dissolution of titanium.^{20,21} Phase transformation of the oxide film occurs (eq. 19). At more positive potentials, the anodic plateau is re-established and extends up to more positive potentials (see section 3.3.2). Due to the high stability of titanium(IV) oxide, the change in pH of the solution does not significantly affect the electrochemical behaviour of tita-

niium (Fig. 3c).



Cyclic voltammograms for Ti-6Al-4V alloy were recorded in the potential range from -1.4 V to 4 V (Fig. 3d). The electrochemical behaviour of this alloy is very similar to that of titanium, with three anodic peaks qualitatively related to the same processes as for Ti. The differences between voltammograms recorded for Ti and Ti-alloy are minor. For the alloy, the current density of peak A_1 is somewhat lower, the effect on the current density of the peak A_2 appears to be smaller, and the peak A_3 recorded at pH 8.0 is more pronounced.

3. 2. Open Circuit Potential and Polarization Resistance Measurements

During stabilization at E_{oc} , the values of electrode potential for all the materials investigated shift towards more positive values with time until stable values are established. These E_{corr} values are presented in Fig. 4a. For stainless steel 316L E_{corr} is most negative at pH 4.5 (-0.347 V). As the pH of the solution increases to 6.5, it shifts to more positive values up to approximately 70 mV (-0.281 V), and then remains approximately constant with further increase of pH up to 8.5.

The mean values of R_p deduced from linear polarization measurements are given in Fig. 4b. The lowest R_p value for stainless steel in SPS is observed at pH 4.5 (74 $\text{k}\Omega$ cm^2), which indicates the greatest tendency to corrosion.

As the pH increases to 7.5, the value of R_p increases almost three-fold (200 $\text{k}\Omega$ cm^2), indicating that under these conditions a protective layer is formed. With further increase of pH, the value of R_p increases somewhat, then levels off at 211 $\text{k}\Omega$ cm^2 .

The trend of E_{corr} as a function of pH for Ti and its alloy is opposite to that for stainless steel (Fig. 4a). At pH 4.5, the value of E_{corr} for Ti is -0.499 V. With increasing pH, it shifts to more negative values reaching -0.627 V at pH 8.0. For the Ti-6Al-4V alloy, the values of E_{corr} are approximately 100 mV more positive than for Ti metal. The same trend as a function of pH is observed.

Contrary to stainless steel, where a relatively sharp increase of R_p with increasing pH is observed, the R_p values for Ti and its alloy are not significantly affected by pH and remain between 220 and 230 $\text{k}\Omega$ cm^2 for Ti, and between 132 and 148 $\text{k}\Omega$ cm^2 for Ti-6Al-4V alloy (Fig. 4b). The almost two-fold greater values of R_p for Ti prove its superior corrosion resistance to that of its alloy. At pH > 6.5 , the R_p values for Ti and stainless steel are similar.

3. 3. Anodic Potentiodynamic Measurements

Anodic polarization curves were recorded for stainless steel, Ti and Ti-6Al-4V alloy in simulated physiological solution of different pH values (Figs. 5–7). From these curves the following electrochemical parameters are deduced: (i) the breakdown potential (E_b), defined as the potential at which the current density starts to increase abruptly, thus limiting the passive region, and (ii) the span of the passive region ($\Delta E = E_b - E_{corr}$), defined as the potential region between the breakdown potential and corrosion potential determined at the end of stabilization period. The value of E_b was determined as the cross-section of tangential straight-lines at the point of current density increase. Deduced values are presented in Fig. 8.

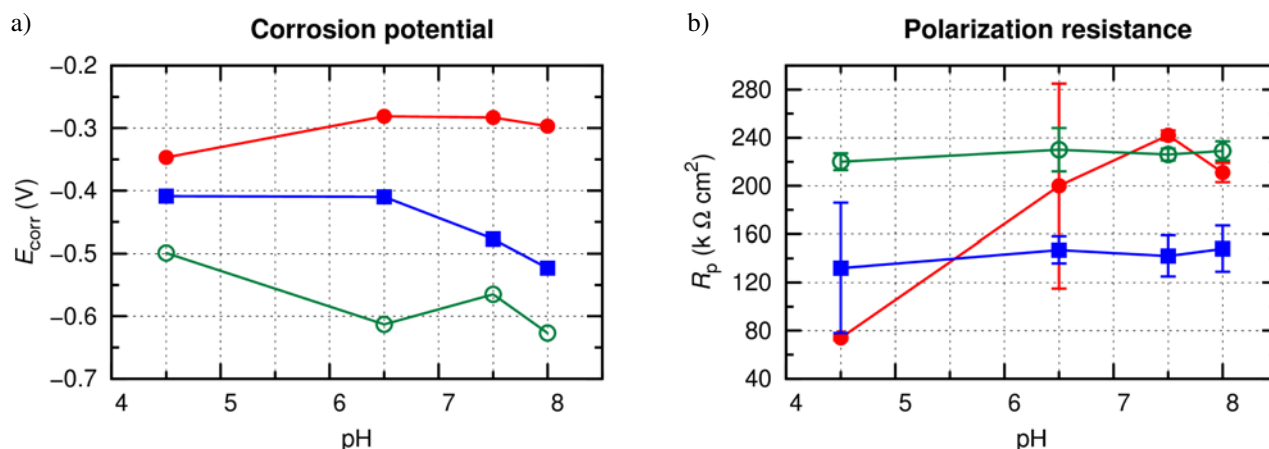


Figure 4. (a) Corrosion potential, E_{corr} , determined at the end of stabilization period, and (b) polarization resistance, R_p , determined from the linear polarization measurements for stainless steel 316L (●), titanium (○) and Ti-6Al-4V alloy (■) as a function of pH value of simulated physiological solution. The values of polarization resistance are given as a mean value \pm standard deviation (denoted by bars).

3.3.1. Stainless Steel 316L

The potentiodynamic polarization curves obtained for stainless steel 316L at different pH values are shown in Fig. 5. As the Tafel region is exceeded, the passive range is established without an active/passive transition. The current density of the anodic curves decreases as the pH increases, indicating the formation of a more protective layer at higher pH. The passive range extends up to E_b , where the current density increases abruptly due to the initiation and propagation of pitting corrosion. The value of E_b is dependent on the pH, ranging from 0.226 V at pH 4.5 to 0.330 V at pH 8.0 (Fig. 8a). The increase of E_b is largest (109 mV) between pH 4.5 and pH 6.5 (from 0.226 V to 0.335 V). The value of E_b does not change significantly with further increase in pH. Therefore, an increase of pH of the solution shifts the value of E_b to more positive values, indicating increased resistance to pitting corrosion. Since both E_{corr} and E_b values are dependent on the pH, the span of the passive region is considered as an objective, representative parameter. The value of ΔE increases by 54 mV from 0.573 V to 0.627 V as the pH increases from 4.5 to 8.0 (Fig. 8b). The width of the passive region thus provides useful information about the tendency to pitting corrosion, i.e. a larger ΔE value indicates better resistance to the initiation of pitting corrosion.

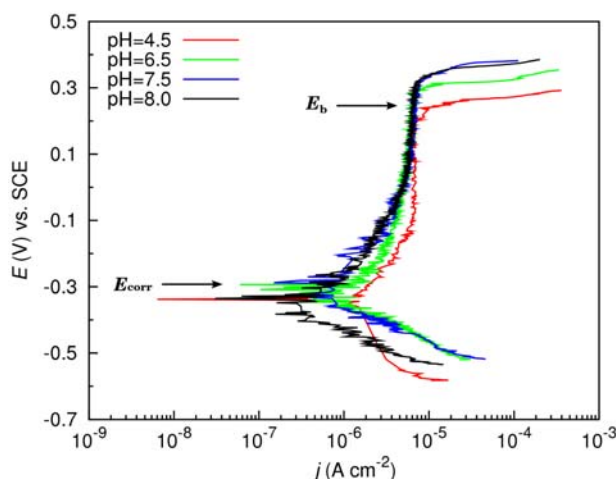


Figure 5. Anodic potentiodynamic curves recorded for stainless steel 316L in simulated physiological solution of different pH values (4.5, 6.5, 7.5 and 8.0). $dE/dt = 1$ mV/s. Examples of determination of corrosion and breakdown potentials are presented by arrows.

3.3.2. Titanium Metal and Ti-6Al-4V Alloy

Anodic potentiodynamic polarization curves recorded for titanium in simulated physiological solutions of different pH values are presented in Fig. 6. The values of the characteristic electrode potentials and cathodic and anodic current density are not affected significantly by the

change in pH. Following the Tafel region, the first anodic plateau is established, related to the formation of titanium sub-oxides as explained in section 3.1.2. At 1.5 V, the second anodic plateau is related to the complete transformation to TiO_2 . As the potential increases further, the current density remains constant at low values in the range of 10^{-6} A cm^{-2} . In contrast to stainless steel, the oxide film formed on titanium is not susceptible to the breakdown of passivity. No pitting corrosion was observed up to a potential of 8.0 V; values of E_b and ΔE could therefore not be determined.

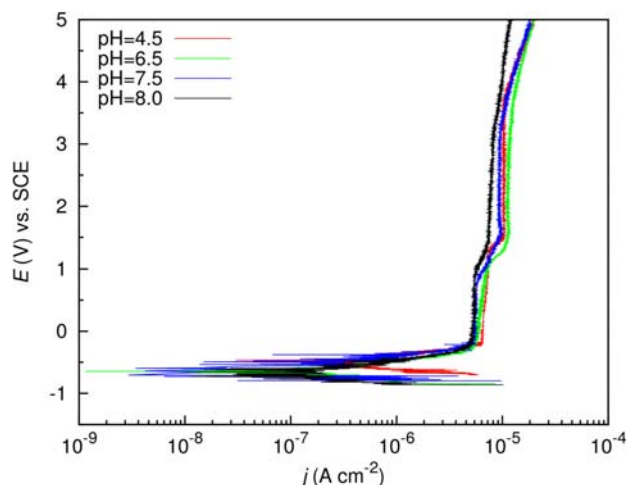


Figure 6. Anodic potentiodynamic curves recorded for Ti in simulated physiological solution of different pH values (4.5, 6.5, 7.5 and 8.0). $dE/dt = 1$ mV/s.

In the potential range from -1 V to 1 V the electrochemical behaviour of the Ti-6Al-4V alloy (Fig. 7) is very similar to that of titanium (Fig. 6). The transition to the second anodic plateau at 1.0 V is not so pronounced for the alloy. The current density remains approximately constant up to 3.5 V when it starts to increase. The third anodic plateau, with values of current density in the range of 10^{-4} A cm^{-2} , extends from 4.0 V to 6.4 V. At more positive potentials, at the E_b , the current density increases abruptly due to passivity breakdown and initiation of pitting corrosion. This process substantially differentiates Ti from its alloy. Whereas no pitting corrosion can be detected on Ti in this potential range, the Ti-6Al-4V alloy is susceptible to localized corrosion attack at potentials more positive than 6.4 V. Compared to stainless steel, the E_b values are located within a narrower range (31 mV), between 6.486 V and 6.796 V for pH values of 4.5 and 8.0 (Fig. 8b). Again, the values of ΔE are considered as a function of pH (Fig. 8b). At higher pH, the values of ΔE increase by 38 mV, from 6.890 V to 7.270 V, a somewhat narrower range compared with stainless steel (54 mV). It is noteworthy that, since the potential established in the body is less than 1 V,¹ initiation of pitting corrosion of the Ti-6Al-4V alloy is unlikely to occur.

The higher susceptibility of the Ti-6Al-4V alloy to localized passivity breakdown than that of Ti may be explained by the presence of the alloying elements, aluminium and vanadium, which both show a narrower potential range of stability (Figs. 3a, b) than titanium. Their presence obviously plays an important role in the stability of the passive film and may be detrimental in terms of resistance to pitting corrosion at high positive potentials.

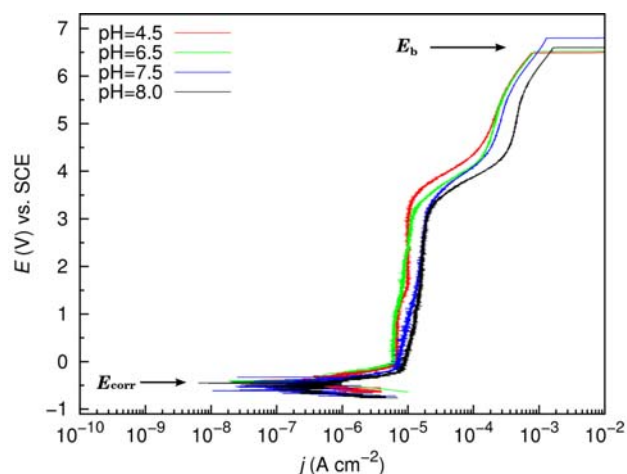


Figure 7. Anodic potentiodynamic curves recorded for Ti-6Al-4V alloy in simulated physiological solution of different pH values. $dE/dt = 1$ mV/s. Examples of determination of corrosion and breakdown potentials are presented by arrows.

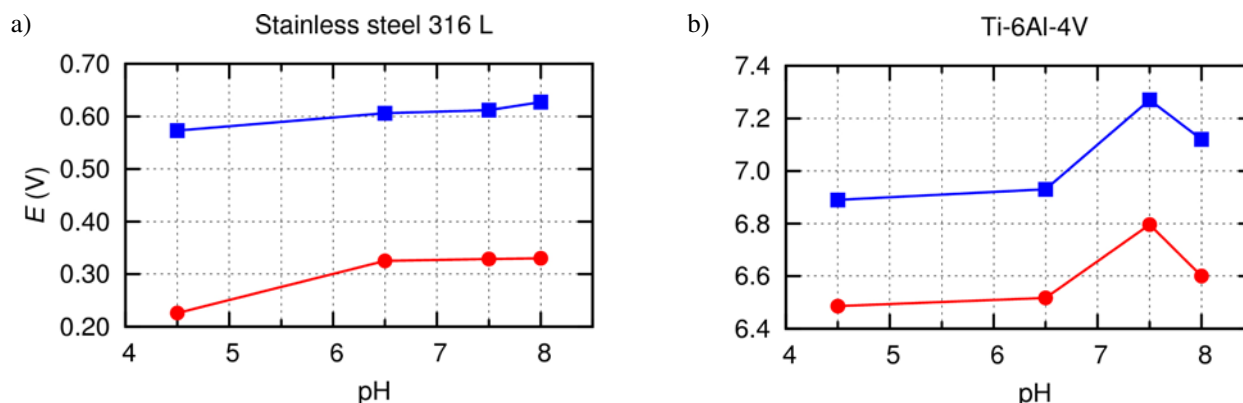


Figure 8. Breakdown potential, E_b , (●) and the width of the passive range $\Delta E (E_b - E_{corr})$ (■) determined from the potentiodynamic polarization curves for (a) stainless steel 316L, and (b) Ti-6Al-4V alloy as a function of pH value of simulated physiological solution.

3. 4. Determination of Metal ion Release

Since the effect of pH on the corrosion resistance is now recognized by the electrochemical measurements, the effect of pH value on the stability of stainless steel and the Ti-6Al-4V alloy was further investigated through an *in vitro* study of biodegradation of these materials in simulated physiological solution of two different pH values, 4.5 and 7.5. The concentrations of the released metal ions (Fe, Cr,

Ni, Mo, Ti, Al and V) were determined as a function of immersion time using inductively coupled plasma mass spectroscopy (ICP-MS). Simulated physiological solution contains various chlorides, sulphate, glucose, sodium, potassium, etc, which can serve as a source of polyatomic interferences. To reduce these interferences from the sample matrix the octopole reaction system was used.

3. 4. 1. Metal ion Release from Stainless Steel 316L

The concentrations of metal ions (Fe, Cr, Ni and Mo) released from stainless steel in SPS at pH 4.5 and pH 7.5 are presented in Fig. 9. Iron is released in the highest concentration, approximately 30-fold higher than the concentration of nickel, the next most dissolved metal. The concentrations of released metal ions decrease in the following order: Fe > Ni > Mo > Cr. For all four metals, the concentrations of released ions are higher at lower pH, again confirming that the degree of dissolution in simulated physiological solution is higher in a more acidic environment. At pH 4.5, the concentration of dissolved iron, and also chromium and molybdenum, increases steadily with time of immersion. For nickel, the values level off after approximately 10 days. At higher pH, the concentrations of released iron, nickel and molybdenum ions level off after 5 days. For chromium, however, a steady increase with time is observed.

The passive film on stainless steel is formed mainly of iron and chromium oxides.^{11–15} Whereas chromium metal forms superficial oxide layers, iron is subjected to active dissolution at lower pH values (Fig. 1). The chemical composition of stainless steel 316L (Fe/Cr18/Ni10/Mo3) is characterized by the following ratios of mass fractions: Fe/Cr = 3.8, Fe/Ni = 6.9, Fe/Mo = 23.0, Cr/Ni = 1.8, Cr/Mo = 6.0 and Ni/Mo = 3.3 (Table 2). When calculating the ratios of

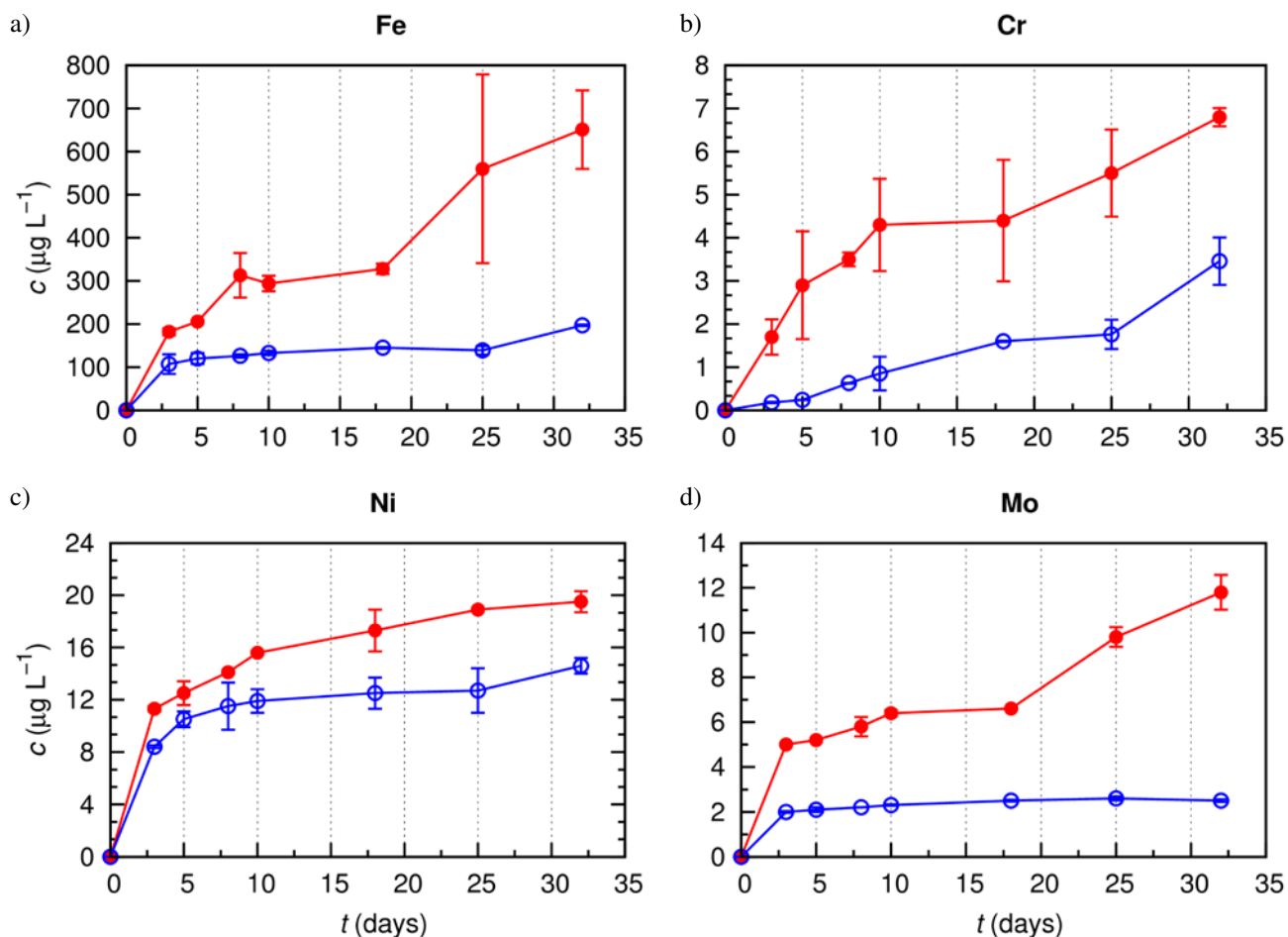


Figure 9. Time dependence of concentration of released metal ions (a) iron, (b) chromium, (c) nickel, and (d) molybdenum measured during immersion of stainless steel 316L in simulated physiological solution of pH values 4.5 (●) and 7.5 (○).

dissolved metal ions measured by ICP-MS, it can be concluded that, at both pH values of simulated physiological solution, iron is dissolved preferentially (Table 2). Whereas in the alloy the ratio Fe/Cr is 3.8, after 32 days of immersion in simulated physiological solution it reaches values of 95.7 and 56.9 at pH 4.5 and pH 7.5. The value is almost doubled at lower pH, showing that, under more acidic conditions, the preferential dissolution of iron is higher. The preferential dissolution of iron relative to that of nickel is lower than for chromium but the same trend is observed. In the case of Fe/Cr and Fe/Ni ratios, the highest values are obtained at pH 4.5, whereas for the Fe/Mo ratio the value is higher at pH 7.5. Chromium is dissolved in concentrations lower than would be expected considering its concentration in the alloy, as evidenced by the lower values of measured Cr/Ni and Cr/Mo ratios compared to theoretical values.

Since nickel is a known allergen, it is noteworthy that the threshold for nickel release below which allergy is not triggered is $0.5 \mu\text{g cm}^{-2} \text{ week}^{-1}$.²² In the present work, the concentration of nickel released during 32 days of immersion of stainless steel in simulated physiological solution is $0.14 \mu\text{g cm}^{-2} \text{ week}^{-1}$ and $0.11 \mu\text{g cm}^{-2} \text{ week}^{-1}$ at

pH values of 4.5 and 7.5, approximately four times lower than the allergy threshold.

Table 2. Ratios of particular elements in the alloy calculated from the chemical composition of stainless steel 316L (Fe/Cr18/Ni10/Mo3) and calculated from the concentrations of metal ions measured by the ICP-MS after 32 days immersion in simulated physiological solution at pH 4.5 and pH 7.5 (Fig. 9).

Metals ratio in the alloy	Metals ratio in the alloy	Ratio of dissolved ions at pH = 4.5	Ratio of dissolved ions at pH = 7.5
Fe/Cr	3.8	95.6	56.9
Fe/Ni	6.9	33.4	13.5
Fe/Mo	23.0	55.2	78.8
Cr/Ni	1.8	0.35	0.24
Cr/Mo	6.0	0.58	1.38
Ni/Mo	3.3	2.30	5.80

3. 4. 2. Metal Release from Ti-6Al-4V Alloy

The quantity of titanium and aluminium released from the Ti-6Al-4V alloy was below the detection limit of

the applied ICP-MS method. Although the determination of titanium is difficult in the presence of high chloride and carbon concentrations due to polyatomic interferences, the most probable reason for the low Ti and Al concentrations is that their dissolution is very low under the experimental conditions used. The formation of stable titanium(IV) and aluminium(III) oxides prevents the release of these ions. Similar results were obtained by Okazaki et al.⁴ The quantities of Ti and Al ions dissolved during immersion in phosphate-buffer saline and 0.9% NaCl solution were below the detection limit of ICP-MS.⁴ On the other hand, released vanadium ions could be detected, although the concentrations were quite low. Similar results are obtained in this work. After 32 days of immersion the concentrations of dissolved vanadium were only 0.76 $\mu\text{g L}^{-1}$ at pH 7.5, and 0.22 $\mu\text{g L}^{-1}$ at pH 4.5 (Table 3).

Table 3. Concentration \pm standard deviation of vanadium released from the Ti-6Al-4V alloy during immersion in simulated physiological solution of pH values 4.5 and 7.5 measured by the ICP-MS.

Immersion time (days)	Concentration ($\mu\text{g L}^{-1}$)	
	pH = 4.5	pH = 7.5
3	<0.02	<0.05
5	0.02 \pm 0.01	<0.05
8	0.06 \pm 0.01	<0.05
10	0.12 \pm 0.08	0.05 \pm 0.10
18	0.15 \pm 0.00	0.22 \pm 0.15
25	0.20 \pm 0.02	0.51 \pm 0.09
32	0.22 \pm 0.01	0.76 \pm 0.02

4. Conclusions

The corrosion behaviour of three orthopaedic materials, stainless steel 316L, titanium and Ti-6Al-4V alloy, and their constituent metals has been studied using electrochemical measurements and biodegradation tests in simulated Hanks physiological solution of different pH values.

Lower corrosion current densities and broader passive regions for titanium and Ti-6Al-4V alloy indicate better corrosion resistance than for stainless steel 316L. The pH value of Hanks solution significantly affects the corrosion resistance of stainless steel, which decreases at lower pH. The large effect of pH is due primarily to iron, since it changes behaviour from passivation to active dissolution with decreasing pH value. In contrast to stainless steel, the pH value does not influence the corrosion behaviour of titanium and Ti-6Al-4V alloy significantly.

Stainless steel 316L and chromium are more corrosion resistant than iron, nickel and molybdenum. The corrosion behaviour of iron is the most affected by pH, while the other three metal components, chromium, nickel and molybdenum, are less affected. Titanium and Ti-6Al-4V alloy show significantly better corrosion resistance than aluminium and vanadium.

Biodegradation tests demonstrated that stainless steel 316L releases more corrosion products into the environment than Ti-6Al-4V alloy. Iron is preferentially released from the alloy. The concentration of released metal ions decreases at higher pH. The concentrations of dissolved titanium and aluminium were below the detection limit, and that of dissolved vanadium was very low.

This study emphasizes the importance of the pH of the physiological solution. In future, investigations will be performed to precise the changes of the pH as a function of conditions in the periprosthetic tissue *in vivo*.

5. Acknowledgements

The financial support of this work provided by the Slovenian Research Agency within the research grant P2-0148 is greatly appreciated. The authors thank Ms. Barbara Kapun for her valuable technical help.

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Povzetek

Kovine in zlitine, ki se uporabljajo v dentalnih in ortopedskih aplikacijah, so *in vivo* izpostavljene različnim kemijskim spojinam in fizikalno-kemijskim pogojem. Eden izmed pomembnih dejavnikov, ki vplivajo na korozijsko obnašanje kovinskih biomaterialov, je pH vrednost okolja, v katerem se ta biomaterial nahaja. Korozijsko odpornost nerjavnega jekla 316L (Fe/Cr18/Ni10/Mo3), titana in titanove zlitine Ti-6Al-4V (Ti90/Al6/V4) smo študirali na osnovi njihovih elektrokemijskih lastnosti in biodegradacije v simulirani fiziološki raztopini pri različnih pH vrednostih (4,5, 6,5, 7,5 in 8,0). Elektrokemijske značilnosti posameznih kovinskih komponent smo raziskovali z uporabo ciklične voltametrije, linearne polarizacije in potenciodinamske polarizacijske metode. Koncentracijo raztopljenih kovinskih ionov, ki se je sproščala med 32-dnevnim testom v simulirani fiziološki raztopini, smo določili z masno spektroskopijo z induktivno sklopljeno plazmo.

Korozijska odpornost nerjavnega jekla 316L je močno odvisna od pH vrednosti fiziološke raztopine v območju od 4,5 do 8,0. Z večanjem pH se odpornost povečuje in koncentracija raztopljenih ionov zmanjšuje. Obnašanje titana in njegove zlitine je skoraj neodvisno od vrednosti pH.