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Metal materials biodegradation: a chronoamperometric study

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The aim of this work is to illustrate the use of a reliable electrochemical technique – chronoamperometry – for the study of the biodegradation process that metal alloys suffer in the human body. The designed *in vitro* experiments, simulating in a short period the situation *in vivo*, can be used to quantify the materials corrosion resistance. Data on the amount of released materials can also be obtained which is valuable information for research on biocompatibility.

1. Introduction

For well-known and well-understood medical reasons, the use of non-living materials in the body is a widespread practice in orthopaedic surgery. Although considerable research has been developed [1–5], mainly with the aim of finding suitable materials for critical situations which could fulfil human-body requirements (e.g. biological acceptance and withstanding of known stresses) and simultaneously be "stable" for indefinite periods, present knowledge raises several questions and a general concern about the medium-term and/or remote physiological effects due to material degradation [6–8].

Metals were the first type of materials to be used, but the effect of the environment on the material was soon realized. Efforts to achieve biological compatibility, adequate mechanical properties and good corrosion-resistance have established certain metal alloys as suitable for orthopaedic implants, namely stainless steel and cobalt- and titanium-based ones. Still corrosion occurs and degradation of the metal alloys in physiological medium is a real problem which must be faced.

It is known that for material destruction the most important reactions are electrochemical in nature and must be taken into account together with the complexity of the body fluids. The fundamental electrochemical concepts to understand and study the phenomena have been outlined elsewhere [9]. The variety of situations (galvanic actions, heterogeneity, stress, etc.) and conditions (pH, temperature, oxygen content, presence of aggressive ions, surface state, etc.) where corrosion can occur requires a careful judgement to choose the technique to study the process and obtain correct information about the behaviour of materials.

Controlled potential techniques are the most reliable methods for the precise electrochemical characterization of metal alloys in different electrolyte environments. When the material (electrode) is forced to follow a given potential programme, which can be a constant value (chronoamperometry) or linearly swept with time (linear potential sweep chronoamperometry, also known as linear sweep voltammetry), the current can be recorded as a function of time, allowing the biodegradation process to be described both qualitatively and quantitatively.

Therefore, the electrochemical tests can be normalized in view of the desired classification of biometal–materials. It was this route proposed by authors concerned with metal alloys used in odontology [10]. Their work also provides the path for further research on the evaluation of corrosion protection efficiency [9, 11] and stimulates the use of the above electrochemical method to characterize the behaviour of other metal alloys and/or other biological environments.

In this work two alloys generally used as orthopaedic implants were studied and the results reinforce that the use of naked metals in the human body cannot be taken as usual practice. The final objective is a contribution for the establishment of reliable methods of testing new materials or new coatings in order to preview their future behaviour *in vivo* and thereby to prevent or to avoid the undesirable effects.

2. Experimental methods and procedure

Typical orthopaedic implants of metallic materials (chromium–cobalt alloy, Howmedica International Inc., Ireland, and stainless steel, A. O. Straumann Institute, Switzerland) were used. Their composition is shown in Table I. The samples were prepared as

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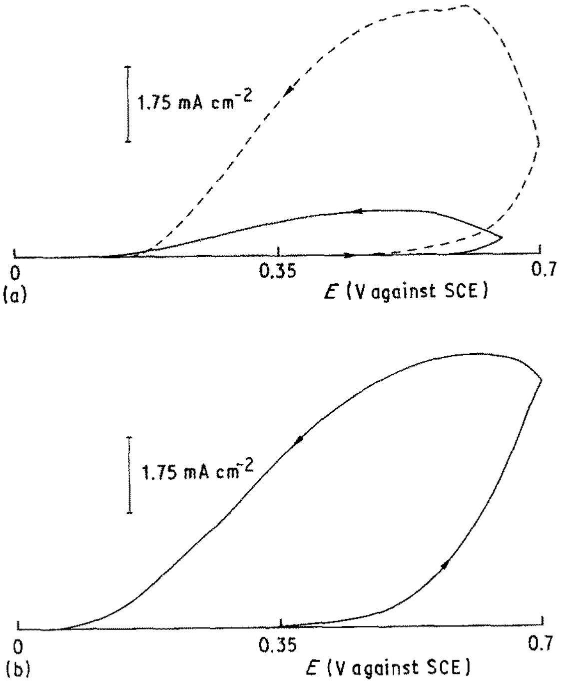


Figure 1 Potentiodynamic polarization curves for stainless steel. (a) Scan to +0.65 V (——) and consecutive scan to +0.7 V (- - -) and (b) typical subsequent scan.

discs with diameters of 5 to 8 mm and thickness 1 to 3 mm.

For the study of the surface finishing effect on the electrochemical behaviour, the exposed cross-section of the electrode was ground flat and polished with fine emery paper to a mirror finish. Subsequently the electrode was prepared for each experiment by hand-polishing with an aqueous suspension of successively finer grades of alumina (Buehler 0.3, 0.075 and 0.05 μm) and carefully rinsed. Vacuum electrode holders [10], for samples without further surface treatment, were used.

The metallic alloy electrodes were mounted in a three-electrode cell with a large-area gold counter-electrode. Potentials were controlled with respect to a saturated calomel electrode (SCE) mounted in a separated compartment and connected via a salt bridge and an adjustable Luggin capillary.

The composiiton of the electrolyte solution, simulating physiological plasma, is given in Table II and it was made up from P.A. reagents with de-ionized, triply distilled water (pH 6.88). The volume used in each experiment was 90 cm^3.

Experiments were carried out at 37 ± 0.1° C by circulating the water bath of a Grant model W14 thermostat through the double wall of the cell. For homogeneity an Ika-Rombinag Ret. stirrer was controlled at 200 r.p.m. Electrochemical studies were performed using a Bank Elektronik Wenking model LB 75L potentiostat, a model VSG 83 waveform generator, and an *X–Y–t* Houston recorder to collect the current transients. Atomoic absorption measurements were made with a Pye-Unicam SP 9 spectrometer associated to a Philips model 910 computer. For the calibration procedure BDH spectrosol standard solutions (1.0 mg cm^{-3}) were used and diluted with the electrolyte.

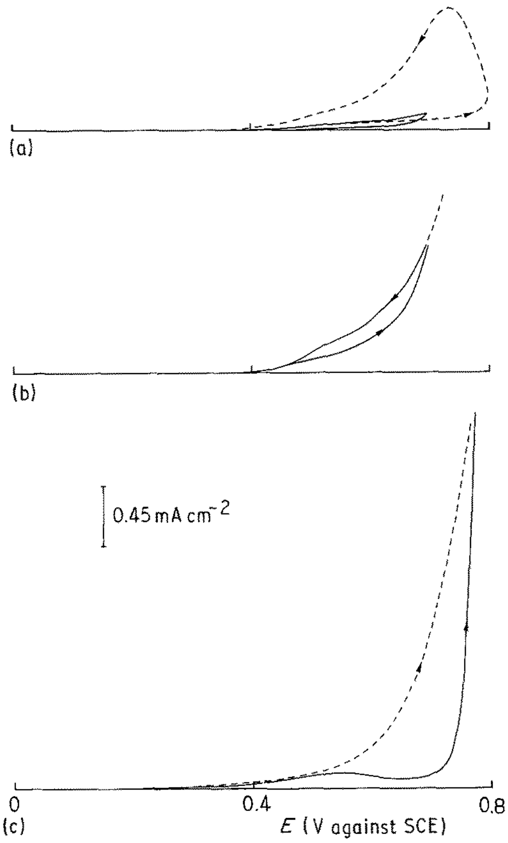


Figure 2 Potentiodynamic polarization curves for Vitalium. (a) Scan to +0.70 V (——) and consecutive scan to +0.8 V (- - -); (b) typical subsequent scan and (c) scans with electrode polished before (——) and after (- - -) constant potential chrono-amperometry.

Samples as originally provided after polishing and after chronoamperometric experiments were observed by scanning electronic microscopy (Jeol, model JSM-T300). SEM coupled with a Tracornorthem TX 1/50-6618 EDS enabled a semi-quantitative materials analysis.

3. Results and discussion

Linear potential sweep chromo-amperometry recorded in artificial plasma, at a 5 mV sec^{-1} sweep rate, is

TABLE I Alloy compositions

	Stainless steel (%)	Vitalium (%)
Chromium	16–18	27.5–28.5
Nickel	10–14	1
Molybdenum	2–3	5.5–6.3
Manganese	2	0.6–0.8
Iron	Balance	0.2–0.5
Carbon	0.003	0.6–0.8
Silicon	10	0.7–0.9
Cobalt	–	Balance

TABLE II Electrolyte composition

Salt	g dm^{-3}
NaCl	6.800
$CaCl_2$	0.200
KCl	0.400
$MgSO_4$	0.100
$NaHCO_3$	2.200
Na_3PO_4	0.126
NaH_2PO_4	0.026

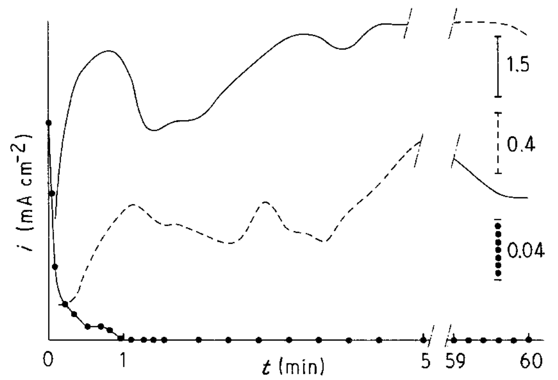


Figure 3 Current plotted against time for stainless steel chronoamperometry at constant potential: (——) 760 mV, (- - -) 690 mV and (· · · ·) 550 mV.

shown in Fig. 1 for stainless steel (0 to 0.7 V against SCE) and in Fig. 2 for Vitalium (0 to 0.8 V against SCE).

Although the potential domain where passivation exists is similar for both materials, the first potential scan shows a better corrosion resistance behaviour in the Vitalium case, since it presents considerably lower anodic currents.

Second scans provided further evidence: the passivation anodic potential limit decreases significantly for stainless steel and higher currents were observed. After several potential cycles the current response can be considered reproducible, as seen in Figs 1b and 2b. The large hysteresis presented by stainless steel shows that after the occurrence of corrosion it is meaningless to refer to a passivation potential range. This is not the case for Vitalium, where the current decreases, in the reverse scan, to a negligible value very close to the passivation anodic potential limit.

When samples were polished as described in the previous section, a reproducible potentiodynamic polarization curve was observed as illustrated in Fig. 2c. However, after constant potential chronoamperometry higher than the anodic limit the material was so degraded that the insufficiency of the same surface treatment was noticed by the non-observance of the material initial corrosion resistance.

The shape of the voltammogram differs markedly from multiple potential cycled material (Fig. 2b). For a freshly polished sample the abrupt increase in current, when the anodic potential limit was reached, must be noted.

By chronoamperometry at constant potential the degradation process evaluation can be obtained in a short time and simulates the effect of material ageing inside the human body.

TABLE III Conditions for the chrono-amperometric experiments

Experiment	Electrode material	Potential (mV)	Time (h)
1	Stainless steel	550	1
2	Stainless steel	690	1
3	Stainless steel	760	1
4	Vitalium	500	1
5	Vitalium	600	1
6	Vitalium	750	1
7	Vitalium	750	2

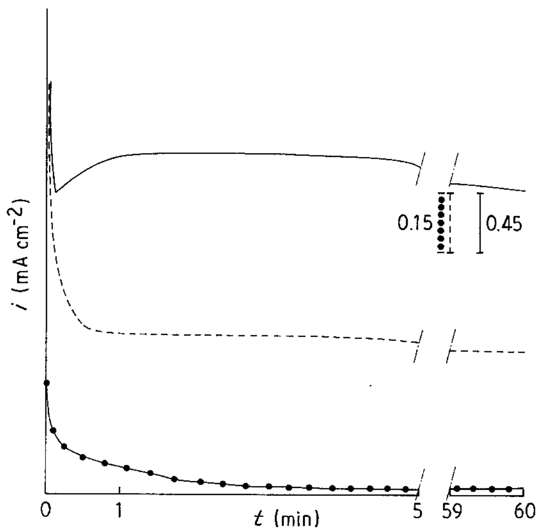


Figure 4 Current plotted against time for Vitalium chronoamperometry at constant potential: (——) 750 mV, (- - -) 600 mV and (· · · ·) 500 mV.

Based on the polarization curves shown in Figs 1 and 2, the potentials and times presented in Table III were chosen.

The current evolution for these experiments is presented in Figs 3 and 4. Although the Vitalium gives rise to smaller currents than the stainless steel, some of the features of the currents are similar. For potentials close to the anodic limit of passivation the current decreased rapidly to or nearly to zero. For higher potentials the current after an initial period reached a plateau or it decreased slightly.

The corrosion process for stainless steel is much more intense, as shown by the above results and by the observation of the material after electrolysis. In fact, the surface of a sample ready to be used in orthopaedic surgery looks like Figs 5a and b (where some degradation is already noticed). After 1 h of electrolysis, at 760 mV, the effect of the corrosion process is as shown in Fig. 5c. Fig. 6a presents an unused implant and Fig. 6b a Vitalium electrode after being polished and submitted to 750 mV against SCE for 2 h.

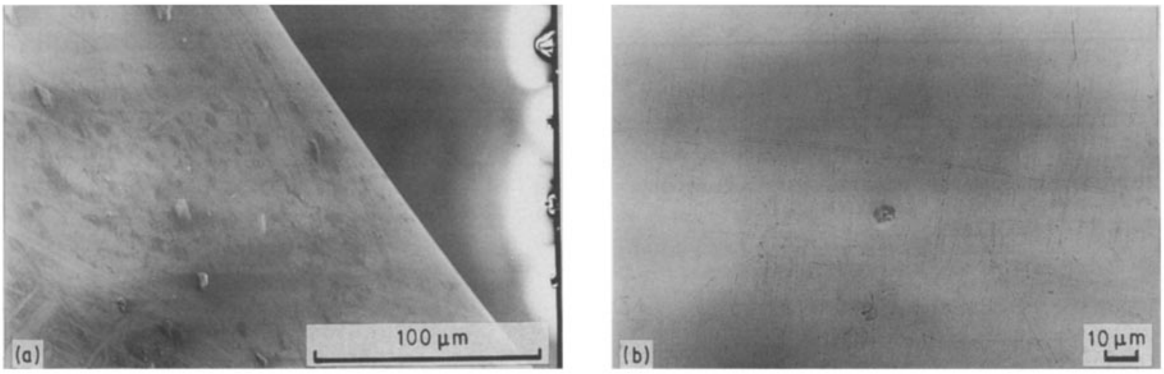
Atomic absorption spectrometry enabled the evaluation of the corrosion products in the electrolyte solutions. For experiments with stainless steel the reaction of released ions with artificial plasma was intense and a soft, solid produce was formed. However, this was readily dissolved in nitric acid and this was the procedure followed to prepare samples for atomic absorption measurements.

The amounts determined in the electrolyte solutions are shown in Table IV. All of the values are much

TABLE IV Atomic absorption analysis (p.p.m.)

Experiment	Iron	Nickel	Chromium	Cobalt
1	ND	ND	ND	
2	6.5	1.6	2.5	
3	9.4 (~ 35)	5.2 (~ 9)	4.8 (~ 14)	
4			0.2	0.2
5			0.5	0.5
7			1.7	2.0

ND, not detected.



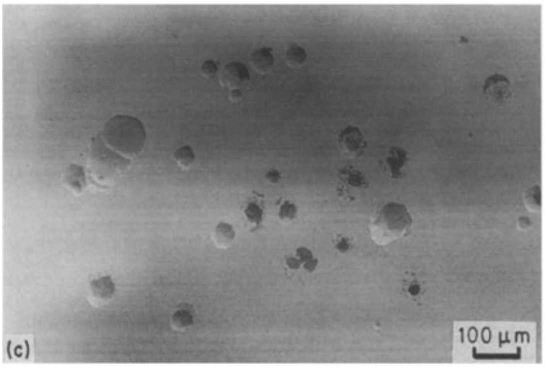


Figure 5 SEM micrographs of stainless steel: (a) and (b) used for orthopaedic surgery and (c) after 1 h of chrono-amperometry at 760 mV.

higher than the normal content of any physiological fluids [12].

In spite of the lack of precision in the current values for the first few seconds of chronoamperometry (Figs 3 and 4), the charges involved in the process for the initial 5 min suggest much larger amounts for electrolysis 3 (as indicated in parentheses). However, there is an inversion in the magnitude of the current for electrolyses 2 and 3 during the major part of the process, and therefore the values of iron, nickel and chromium in the electrolytes used with stainless steel follow the expected trend. At higher potentials the corrosion products on the electrode surface hinder further local corrosion.

On the other hand, Vitalium shows a slower but regular corrosion and the amount of materials in the electrolyte is proportional to the electrolysis charge.

A semiquantitative test of the surface chemical composition after electrolysis at the higher potential was carried out and, although the results need to be regarded with caution as they refer only to small portions of the overall electrode area, namely a large pit and a non-corroded area, they agree with the values from the atomic absorption analysis (see Table V).

4. Conclusions

Electrochemical experiments described and illustrated in this work for two kinds of biomaterials enable the evaluation and comparision of the behaviour of different materials in media which, carefully chosen, can simulate biological fluids. Followed for a short time, the biodegradation process and the materials released by metal alloys can be evaluated. These are equivalent to the reaction in a real situation for longer periods.

A systematic study of this kind provides data to study the toxicity of biomaterials and, with cytocompatibility and specific biocompatibility research [11, 13], is probably the only way to answer questions about the magnitude and clinical significance of the corrosion of metallic implants.

TABLE V Semiquantitative analysis of stainless steel (wt %)

	Corroded area	Non-corroded area
Chromium	25.5	18.2
Nickel	8	15.2
Iron	66.5	66.6

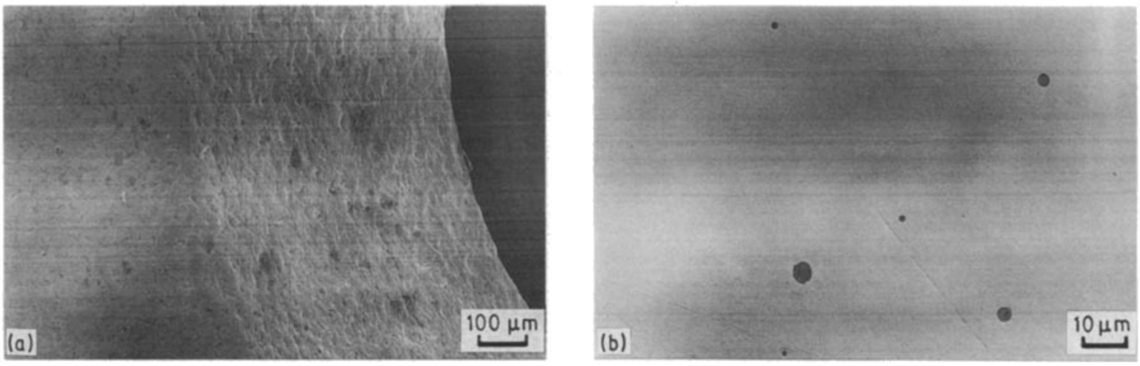


Figure 6 SEM micrographs of Vitalium: (a) as used for orthopaedic surgery and (b) polished and after 1 h chrono-amperometry at 750 mV.

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