The influence of complexing agent and proteins on the corrosion of stainless steels and their metal components

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The present work is devoted to the problem of biodegradation of orthopaedic implants manufactured from stainless steel. *In vitro* simulations of the biocompatibility of two types of stainless steel, AISI 304 and AISI 316L, and their individual metal components, i.e. iron, chromium, nickel and molybdenum, were carried out in simulated physiological solution (Hank's) containing complexing agents. Knowledge of the effects of the chemical and biological complexing agents, EDTA and proteins, respectively, on the corrosion resistance of a metal should provide a better understanding of the processes occurring *in vivo* on its surface. The behavior of stainless steels and metal components was studied under open circuit and under potentiostatic conditions. The concentration of dissolved corrosion products in the form of released ions was determined by differential pulse polarography (DPP) and atomic emission spectrometry using inductively coupled plasma (ICP-AES). The composition of solid corrosion products formed on the surface was analyzed by energy dispersive X-ray spectroscopy (EDS) and their morphology was viewed by scanning electron microscopy (SEM). The addition of EDTA and proteins to physiological solution increased the dissolution of pure metals and stainless steels. The effect of particular protein differs on different metals and alloys.
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Introduction

The electrochemical properties of stainless steel are important for its performance as a biomedical orthopaedic material, owing to its ability to spontaneously passivate and maintain passivity under physiological conditions. The introduction of metal alloys into a human body is not completely innocuous, since they may suffer corrosion. It is well known that chloride solutions are among the most aggressive environments. In the case of actively functioning artificial joints, such as artificial hips, wear of metallic material may also occur. Corrosion and wear are therefore responsible for the release of toxic and potentially carcinogenic metallic species, like nickel and chromium, from the implant surface. Released species either accumulate in the tissues surrounding the implant, or are transferred by body fluids and then accumulate in the liver, spleen, etc. [1, 2].

Electrochemical methods are commonly used for evaluating the biocompatibility of metallic materials [3]. In the majority of studies sodium chloride solution or more complex saline solution, such as Ringer's or Hank's solution, is used as an electrolyte. However, these solutions do not entirely simulate the environment in a human body. The most important entities missing in *in vitro* studies of metal–tissue interactions are proteins. Relatively few studies have dealt with the effect of proteins on the corrosion behavior of metals [4–8]. Brown and Merrit [4] have demonstrated that stainless steels are subjected to pitting corrosion in the presence of proteins. Samitz and Katz [5] noted that body fluids such as blood and sweat promote the release of nickel from stainless steels. Yang and Black [6] determined the percentage of chromium, cobalt, and nickel that bind to murine serum proteins. Woodman *et al*. [7] studied metal–protein complexes using gel chromatography. Results showed that the predominant forms of corrosion products of nickel and chromium are metallo–organic complexes with proteins. Clark and Williams [8] have demonstrated that proteins significantly increase the dissolution of cobalt and copper.

The purpose of the present electrochemical investigation was to evaluate the corrosion resistance of stainless steels AISI 304 and AISI 316L, as well as their metal constituents, iron, chromium, nickel and molybdenum, in physiological solution containing EDTA or the following bovine serum proteins, albumin, γ-globulin, transferrin and fibrinogen. The dissolved corrosion products were determined by differential pulse polarography (DPP) and

atomic emission spectrometry using inductively coupled plasma (ICP-AES), and the surfaces analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).

Materials and methods

The materials used in this study were obtained from various sources: Fe, Ni, Cr and Mo (all 99.9 wt %) from Metalle und Materialien GmbH, Nürnberg, Germany, AISI 304 from Goodfellow, Cambridge, UK, and AISI 316L from Protek, Bern, Switzerland.

The test specimens were cut into discs of 15 mm in diameter. The specimens were abraded with SiC emery paper down to an 800-grit. Two groups of experiments were carried out. In the first group the backside of the sample was covered with a lacquer varnish, leaving only a given specimen area exposed to the test solution. The specimen was immersed in test solutions under open circuit conditions. After a set period of time, the concentration of released metal ions was measured in aliquots by DPP in the case of iron and by ICP-AES in the case of nickel and molybdenum. DPP was the better analytical technique in the case of iron owing to its ability to determine the valences of soluble species. In the case of nickel and molybdenum only Ni(II) and Mo(VI) species, respectively, were expected, therefore ICP-AES was used. The composition of solid corrosion products formed on the surface was analyzed using an EDS LINK ISIS spectrometer and their morphology was investigated by using an SEM JEOL JSM 5800 instrument. In the second group of experiments the specimens were treated potentiostatically. Using a drop of conducting paste, electrical contact with the connecting wire was made at the rear side of each disc. This was then covered with a lacquer varnish and the wire protected by a glass tube. Such a specimen served as a working electrode and was placed in solution with a graphite counter electrode and saturated calomel (SCE) reference electrode. In the course of potentiostatic treatment the concentration of released metal ions was measured in aliquots by DPP in the case of iron, and by ICP-AES in the case of nickel, molybdenum and alloys.

Polarographic measurements were performed using an EG&G PAR PC-controlled polarograph Model 394 with an EG&G PAR polarographic cell Model 303A and a stirrer Model 305. The system contained a dropping mercury working electrode, a Ag/AgCl reference electrode and a Pt auxiliary electrode. As the supporting electrolyte for determining Fe(II) and Fe(III) ions, 0.2 M sodium pyrophosphate at pH = 9 was used (Merck, Darmstadt, Germany). Experimental conditions used in polarographic experiments were as follows: initial potential -0.1 V, final potential -1.5 V, scan rate (dE/dt) 12 mV/s, dropping time 0.5 s, pulse height 50 mV, temperature 20 °C, purging time 240 s and deaerating gas N_2. Quantitative analysis was performed using calibration curves [9].

Spectrometric measurements were performed on a Perkin–Elmer Plasma 40 emission spectrometer, at wavelengths of 238.204 nm for iron, 205.55 nm for chromium, 221.647 nm for nickel and 202.030 nm for molybdenum. The plasma was operated at a power of 1.0 kW and a frequency of 40 MHz, with argon as the coolant gas at a flow rate of 15 $dm^3\,min^{-1}$, and a nebulization flow rate of 1 $dm^3\,min^{-1}$. Quantitative analysis was performed using calibration curves.

Cyclic polarization curves were recorded by using an EG&G PAR PC-controlled potentiostat Model 273 with M270 computer program. Electrode potentials were measured against an SCE reference electrode. The potential was increased at a scan rate of 20 mV/s.

The experiments were performed in a simulated physiological solution (Hank's) (8 g/l NaCl, 0.40 g/l KCl, 0.35 g/l $NaHCO_3$, 0.25 g/l $NaH_2PO_4 \times 2H_2O$, 0.06 g/l $Na_2HPO_4 \times 2H_2O$, 0.19 g/l $CaCl_2 \times 2H_2O$, 0.41 g/l $MgCl_2 \times 6H_2O$, 0.06 g/l $MgSO_4 \times 7H_2O$, 1 g/l glucose) with the addition of complexing agent, 0.05 M EDTA (Merck, Darmstadt, Germany), or proteins – 5 g/l albumin, 2.5 g/l γ-globulin, 0.3 g/l fibrinogen or 0.1 g/l transferrin (all from bovine serum, Fluka, Buchs, Switzerland). The concentration ratios of proteins used correspond to those in serum.

Results

Behavior of pure metals under open circuit conditions

The behavior of iron, nickel and molybdenum was studied over a period of up to 19 days, under open circuit conditions in physiological solution containing EDTA or proteins, at pH = 7.8. The concentrations of released metal ions were measured by DPP and ICP-AES as a function of time. After the experiment the surface of the metal samples was investigated by SEM and analyzed by EDS. The dissolution of chromium at open circuit potential could not be measured due to its excellent corrosion resistance, with the concentrations of Cr-ions being below the limit of detection (LOD).

In physiological solution an immediate oxidation of iron to Fe(II) or Fe(III) occurred, leading to the precipitation of red-brown $Fe(OH)_3$ [10] which partially precipitated at the specimen surface and partially accumulated at the bottom of the cell. Due to its formation the concentration of dissolved Fe-ions was below the LOD. With the addition of EDTA, the concentration of Fe(II) and Fe(III) ions in the solution increased drastically (Fig. 1). At the same time the amount of precipitate decreased. The concentration of Fe(II) ions was somewhat higher than that of Fe(III). Generally, the increase in concentration was not linear with time, probably due to partial adsorption of corrosion products on the surface of the experimental vessel. After approximately 10 days the concentration of Fe(III) ions stabilized, probably as a consequence of the formation of precipitated product. In physiological solution containing proteins the concentration of dissolved iron was lower than that measured in EDTA-containing solution. Only the concentrations of Fe(III) ions were above the LOD. Although the differences in concentrations of Fe(III) ions between individual proteins were relatively small, dissolution was lowest in a solution containing albumin, following by that containing fibrinogen, γ-globulin and transferrin, respectively. After approximately 10 days the precipitation of a red-brown product was observed. The morphology and composition of the

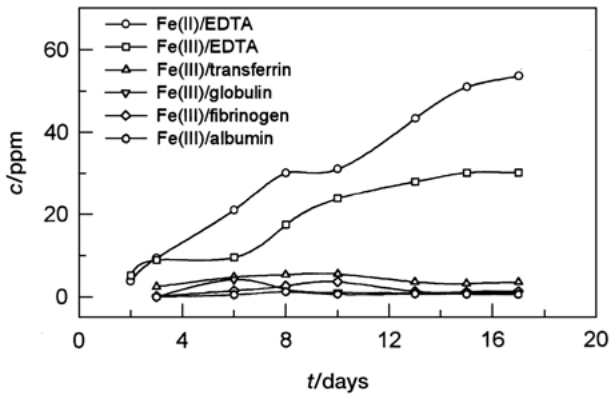

Figure 1 The concentration of dissolved Fe as a function of immersion time of Fe metal in physiological solution (PS) with the addition of EDTA and various proteins. The concentration of dissolved ions was measured by DPP.

specimen surface after the experiment are presented in Fig. 2. The surface of an iron specimen exposed to physiological solution was covered by a black layer, probably corresponding to Fe_3O_4 (Fig. 2(a), and (b)). On top of this layer a certain amount of red-brown corrosion product was precipitated. EDS analysis showed that this product consists of a mixture of iron oxide and iron phosphate. In physiological solution containing EDTA the surface was rough due to continuous dissolution (Fig. 2(c)). Obviously the formation of a oxide layer on the surface of iron was suppressed in the presence of complexing agent since the oxygen content in the layer was significantly lower (Fig. 2(d)).

Nickel showed the largest dissolution rate in physiological solution containing EDTA, where a 7-fold greater concentration compared to Ni(II)-ions in other solutions was observed (Fig. 3). Dissolution of nickel in other solutions increased very slowly with time. As for iron, the differences between various proteins were quite small and concentrations decreased in the following order: fibrinogen, albumin, transferrin and γ-globulin. The surface of a nickel specimen exposed to physiological solution showed small clusters of corrosion products identified by EDS as a mixture of nickel oxide and nickel phosphate (Fig. 4(a), and (b)). The addition of EDTA caused pitting corrosion of nickel (Fig. 4(c)) and no nickel oxide was detected at the surface (Fig. 4(d)).

Molybdenum corroded most rapidly in solution containing EDTA followed by that containing transferrin (Fig. 5). In the presence of fibrinogen, albumin and γ-

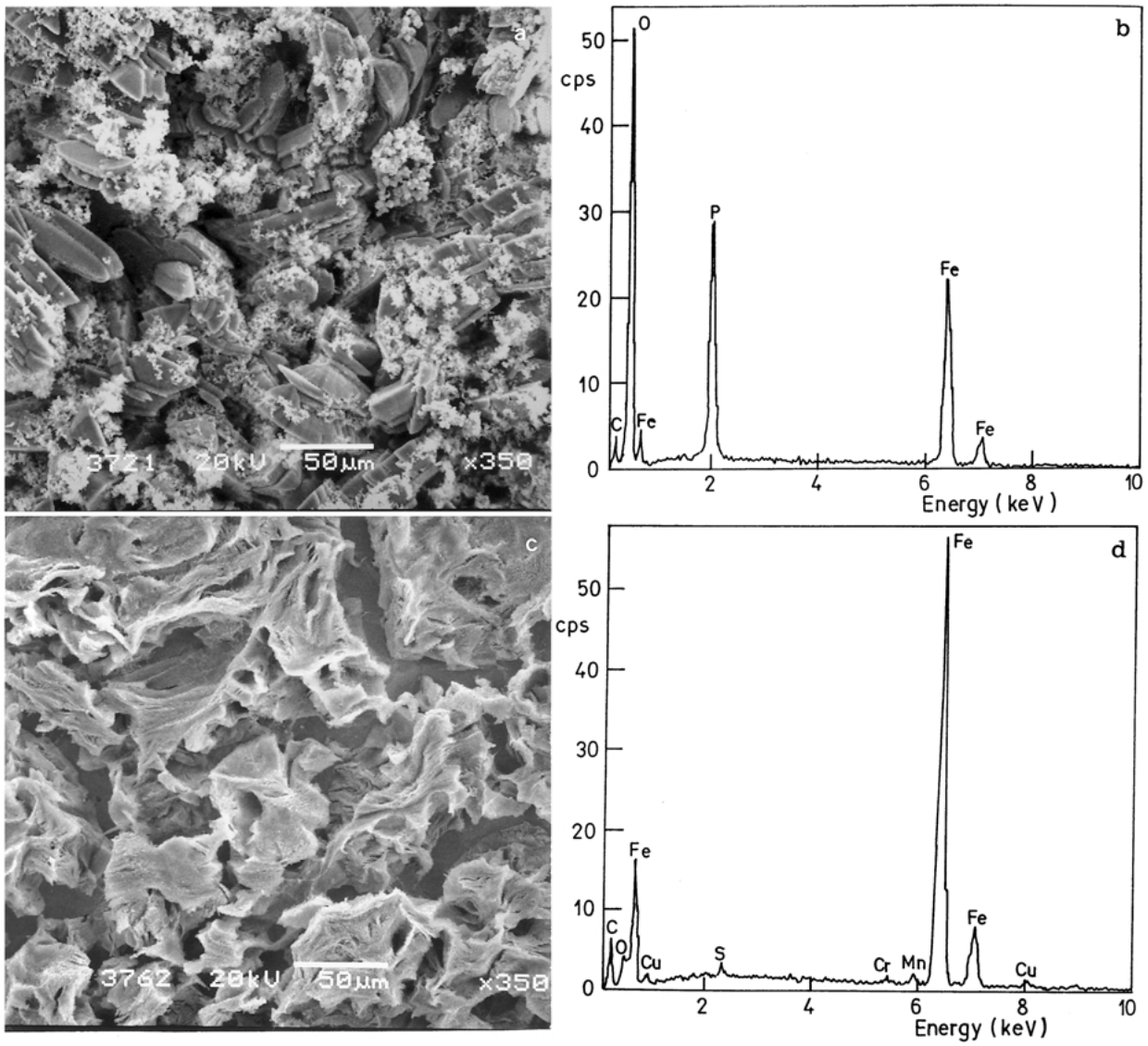

Figure 2 SEM images (a, c) and EDS spectra (b, d) of the corrosion layer formed on the surface of iron after 18 days in (a, b) physiological solution and (c, d) physiological solution containing 0.05 M EDTA.

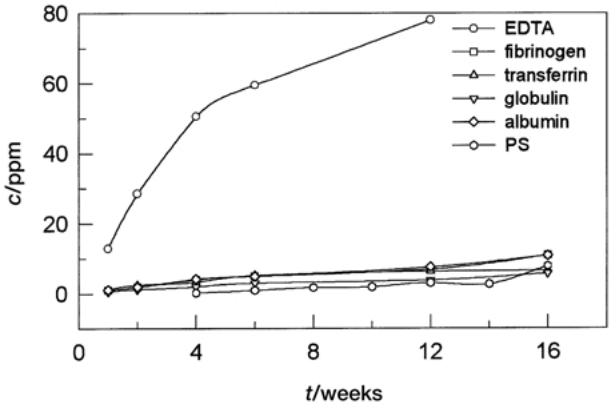

Figure 3 The concentration of dissolved Ni as a function of immersion time of Ni metal in physiological solution (PS) with the addition of EDTA and various proteins. The concentration of dissolved ions was measured by ICP-AES.

globulin much lower dissolution of molybdenum was observed (Fig. 5). The surface of all the samples was covered by a black layer, which was identified by EDS analysis as molybdenum oxide. The addition of EDTA caused a decrease in the oxide content and only pure molybdenum could be detected (results not shown).

Behavior of metals under potentiostatic conditions

Cyclic voltammograms of iron were recorded on various solutions in the potential range -1.0 to -0.26 V (Fig. 6(a)). The lowest current densities were measured in pure physiological solution. With the addition of proteins the anodic current density increased in the following order: transferrin, fibrinogen, γ-globulin and albumin. The most significant increase in anodic current density occurred with the addition of EDTA. Contrary to other solutions, an anodic peak formed at -0.62 V, In physiological solution the surface of the sample was black, probably due to the formation of a thin layer of Fe_3O_4 [10]. At the beginning of the experiment the solution was pale yellow and a white solid product was formed. In the course of prolonged oxidation at -0.26 V the solution turned to yellow-green and a solid green-black product was formed. In physiological solution containing EDTA the iron surface underwent pitting corrosion accompanied by coloration of the solution to intense orange. Fig. 6(b) shows the concentrations of Fe(II) and Fe(III) ions in various solutions given as a function of polarisation time at a selected potential, i.e. -0.26 V. At potential values lower than -0.26 V no measurable concentration of Fe

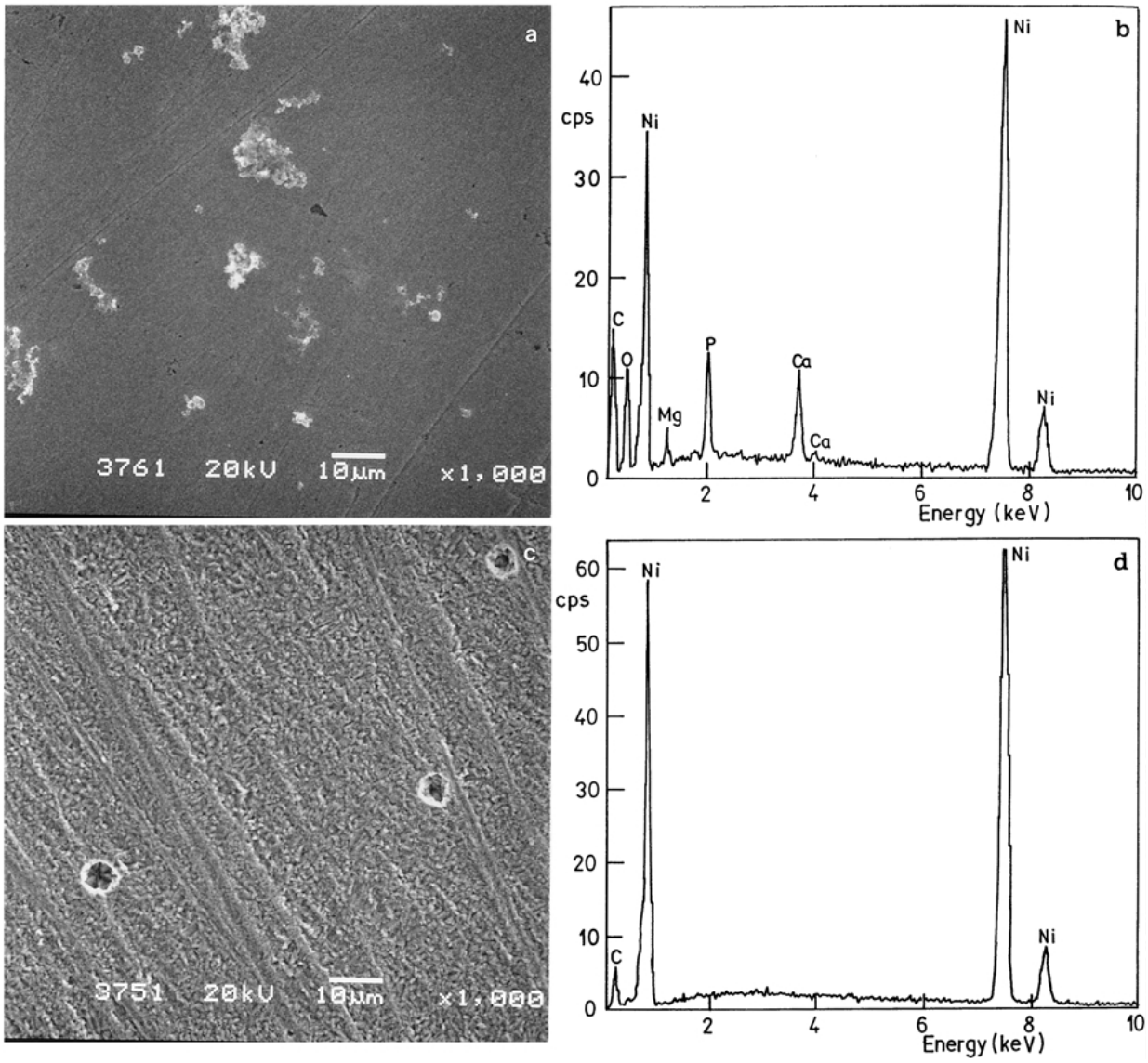

Figure 4 SEM images (a, c) and EDS spectra (b, d) of the corrosion layers formed on the surface of nickel after 18 days in (a, b) physiological solution and (c, d) physiological solution containing 0.05 M EDTA.

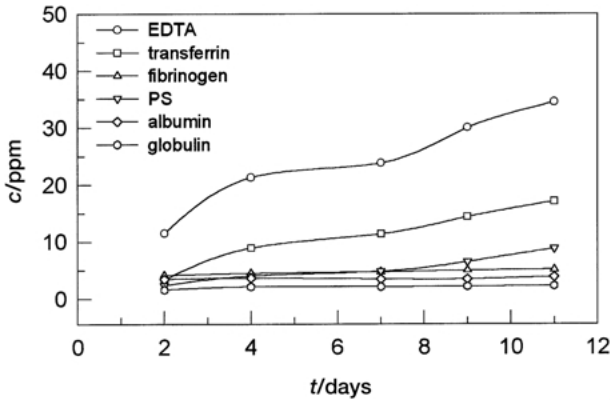

Figure 5 The concentration of dissolved Mo as a function of immersion time of Mo metal in physiological solution (PS) with the addition of EDTA and various proteins. The concentration of dissolved ions was measured by ICP-AES.

ions could be achieved at such a short period of time. The increase in concentration of Fe(II) and Fe(III) ions measured in various solutions follows the increase in current density on the corresponding cyclic voltammograms as a function of the type of complexing agent (Fig. 6(a)).

Cyclic voltammograms of nickel were recorded on various solutions in the potential range -1.0 to 0.2 V (Fig. 7(a)). The passive range is extended between potentials -0.5 and 0.1 V as a consequence of the formation of NiO [10]. With the addition of complexing agents the extent of the passive range decreased. The addition of EDTA did not induce such a significant increase in current density as in the case of iron. On reversing the scan hysteresis was seen, indicating continuous nickel dissolution. The anodic current densities increased from physiological solution, followed by the albumin-, γ-globulin-, transferrin-, fibrinogen- and EDTA-containing solutions. The surface of all nickel samples was apparently intact. The solutions were colorless with only a small amount of a white-greenish solid product. Fig. 7(b) shows the concentrations of dissolved nickel as a function of polarisation time at a selected potential, i.e. 0.2 V, in various solutions. The dissolution of nickel in physiological solution was almost independent of time, whereas in other solutions the concentration increased with time. The concentrations of nickel ions in different test solutions increased in the same sequence as the anodic current densities in cyclic voltammograms (Fig. 7(a)). Compared to iron (Fig. 6), the dissolution of nickel was lower and the order of increase in various solutions of proteins was just the opposite.

Cyclic voltammograms of molybdenum were recorded in various solutions in the potential range -1.0 to 0.2 V (Fig. 8(a)). The order of increase of anodic current density was similar to that of nickel, i.e. the lowest value was observed in physiological solution, followed by albumin-, γ-globulin-, transferrin-, fibrinogen-, with the highest in EDTA-containing solution. The surface of the specimen was in all cases black. In physiological and protein-containing solutions a white product precipitated at the bottom of the cell. With the addition of EDTA, however, no precipitate was observed. At the selected

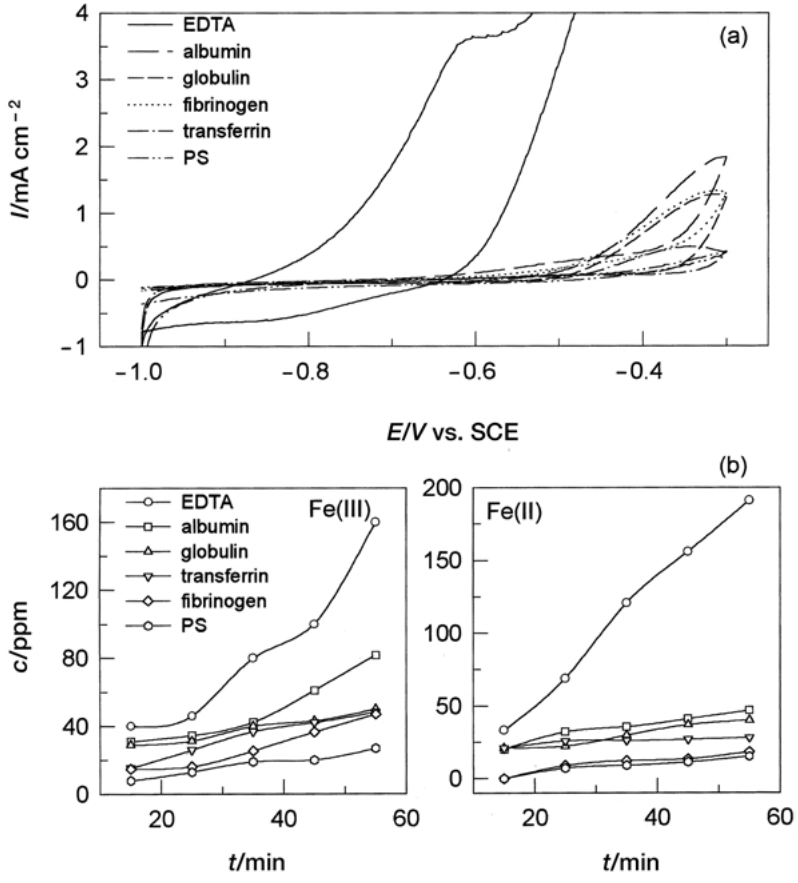

Figure 6 (a) Cyclic voltammograms recorded for iron in physiological solution (PS) with the addition of EDTA and various proteins, $dE/dt = 20\,\text{mV}\,\text{s}^{-1}$. (b) The concentration of dissolved Fe-ions in solution during potentiostatic polarization at -0.26 V as a function of polarization time. The concentrations were measured by DPP.

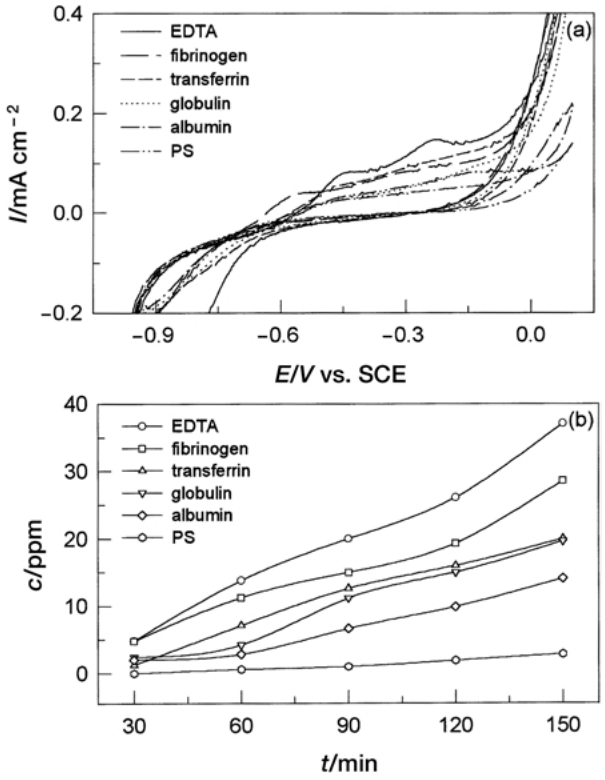

Figure 7 (a) Cyclic voltammograms recorded for nickel in physiological solution (PS) with the addition of EDTA and various proteins, $dE/dt = 20\,\mathrm{mV\,s^{-1}}$. (b) The concentration of dissolved Ni-ions in solution during potentiostatic polarization at 0.2 V as a function of polarization time. The concentrations were measured by ICP-AES.

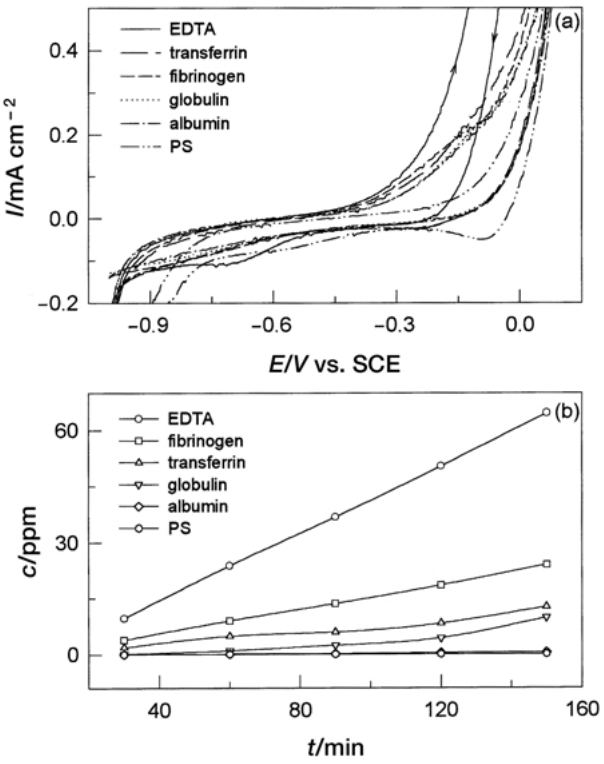

Figure 8 (a) Cyclic voltammograms recorded for molybdenum in physiological solution (PS) with the addition of EDTA and various proteins, $dE/dt = 20\,\mathrm{mV\,s^{-1}}$. (b) The concentration of dissolved Mo-ions in solution during potentiostatic polarization at 0.2 V as a function of polarization time. The concentrations were measured by ICP-AES.

potential, i.e. 0.2 V, the concentration of dissolved molybdenum increased in a sequence similar to the anodic current densities in cyclic voltammograms (Fig. 8(a)). The concentration/time dependence was almost linear in all the solutions except in physiological and albumin-containing solution, where the concentration was time independent and close to the LOD. The concentration of Mo-ions in EDTA-containing solution was much higher than in other solutions.

Behavior of stainless steels under potentiostatic conditions

The effect of the addition of EDTA and various proteins on the electrochemical behavior of stainless steels AISI 304 and AISI 316 was compared to that of the individual metal components described in previous section.

Cyclic voltammograms recorded for AISI 304 stainless steel in various solutions in the potential range from -1.0 to 0.5 V are presented in Fig. 9. The lowest anodic current densities were measured in physiological solution, thus indicating a complete passivation of the surface. Small anodic and cathodic peaks at -0.5 and -0.55 V, respectively, are related to the oxidation and reduction of Fe-oxides, respectively [11]. The passive range is limited by the processes of transpassive oxidation and oxygen evolution at potentials more positive than 0.3 V. On the addition of various proteins the current densities in the anodic cycle slightly increased. The following order of increase was observed: fibrinogen-, transferrin-, γ-globulin- and albumin-containing solution. The most significant increase was observed on the addition of EDTA. Another characteristic feature induced by the presence of complexing agent is the appearance of current hysteresis on scan reversal. The presence of hysteresis indicates that continuous dissolution occurs in the presence of complexing agents. Fig. 9(b) shows the concentrations of dissolved Fe-, Cr- and Ni-species in various solutions given as a function of polarisation time at a potential of 0.5 V. The lowest concentrations were observed in physiological solution. On the addition of proteins the concentrations increased in the following order: fibrinogen, transferrin, γ-globulin and albumin. The concentration of metal ions in EDTA-containing solution increased linearly with time and significantly exceeded the values obtained in protein-containing solutions. The concentration of dissolved chromium was approximately three times lower than that of iron and the concentration of dissolved nickel was somewhat lower than that of chromium. In all solutions the formation of corrosion pits on the surface was observed. In physiological solution the pitting corrosion was accompanied by the formation of a greenish corrosion product, which then precipitated at the bottom of the cell. In the presence of EDTA or proteins no precipitate was formed.

Cyclic voltammograms of AISI 316 stainless steel were recorded in various solutions in the potential range -1.0 to 1.5 V (Fig. 10(a)). Two anodic peaks at -0.4 and 0.7 V, and two cathodic peaks at 0 and -0.5 V were observed. The addition of various proteins and EDTA to physiological solution affects the voltammetric characteristics (Fig. 10(a)). The current density in the anodic cycle increases in the following order: albumin, γ-globulin, fibrinogen, transferrin and EDTA. Fig. 10(b)

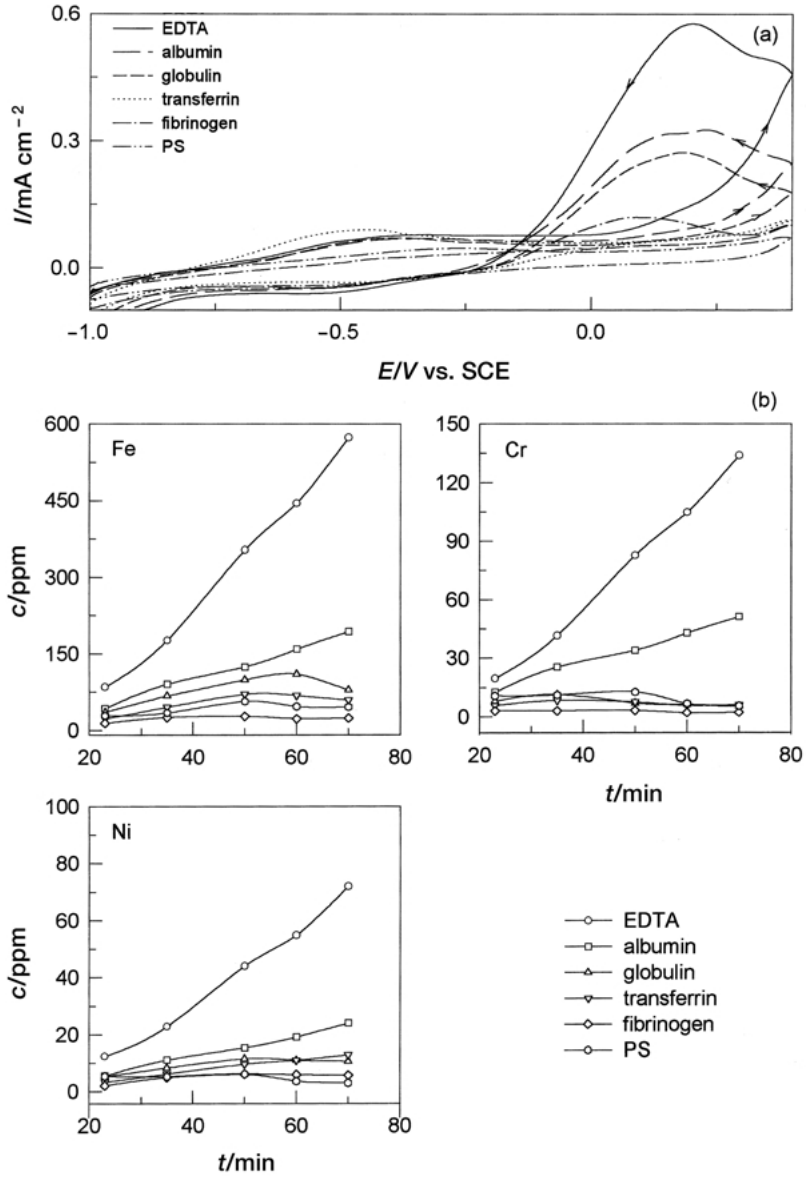

Figure 9 (a) Cyclic voltammograms recorded for AISI 304 stainless steel in physiological solution (PS) with the addition of EDTA and various proteins, $dE/dt = 20\,\mathrm{mV\,s^{-1}}$. (b) The concentration of dissolved Fe, Cr and Ni ions in solution during potentiostatic polarization at 0.5 V as a function of polarization time. The concentrations were measured by ICP-AES.

gives the concentration of dissolved Fe, Cr, Ni and Mo measured during the potentiostatic oxidation at 1.5 V. The lowest concentrations were measured in physiological solution. On the addition of proteins the concentrations increased in the following order: albumin, γ-globulin, fibrinogen and transferrin. Compared to AISI 304 stainless steel, this is almost the opposite order of increase. Common to both types of steel is the most significant dissolution in the presence of EDTA. Generally, the dissolution of iron was the most pronounced, followed by significantly lower concentrations of dissolved chromium, nickel and, finally, molybdenum. After the experiment the surface of the samples remained apparently intact and no precipitation product was observed.

Discussion

On the surface of metals under the condition of open circuit in physiological solution oxide films are formed and, at the same time, metal ions are released into the solution (Figs. 1–5). On the surface of iron a black layer of Fe_3O_4 is formed [10]. Fe(II) and Fe(III) ions are released into the solution and immediately precipitated as a red-brown colored $Fe(OH)_3$ [10]. Nickel oxide is formed on the surface of nickel, whereas in the solution Ni(II)-ions are present. Molybdenum is covered by a layer consisting of molybdenum oxide. At the same time Mo(VI)-ions are released into the solution. The addition of complexing agents affects the formation of oxide layer, as well as of dissolved species. For all three metals the dissolution was enhanced and the formation of oxide layer was inhibited. That was confirmed by EDS analysis, where the oxygen signal in solutions containing complexing agents was reduced and the signal of pure metal was increased. At the same time, the concentrations of metal ions of a particular specimen in the solution increased.

A similar behavior was observed under controled potential conditions (Figs. 6–8). With the addition of complexing agents the current densities increased with respect to physiological solution and the concentrations of released metal ions increased. The comparison of cyclic voltammograms of iron, nickel and molybdenum

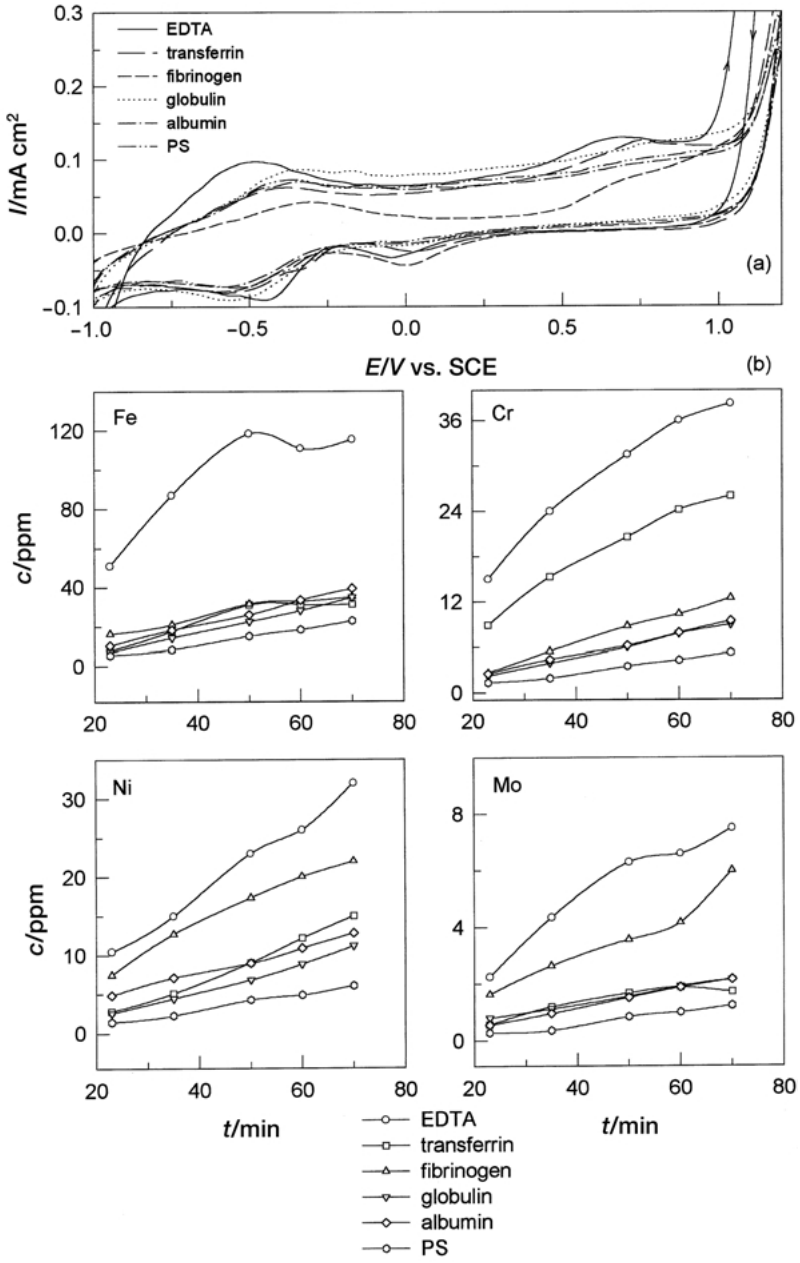

Figure 10 Cyclic voltammograms recorded for AISI 316 stainless steel in physiological solution (PS) with the addition of EDTA and various proteins, $dE/dt = 20\,\text{mV}\,\text{s}^{-1}$. (b) The concentration of dissolved Fe, Cr, Ni and Mo ions in solution during potentiostatic polarization at 1.5 V as a function of polarization time. The concentrations were measured by ICP-AES.

shows the different corrosion resistance of these metals. As a criterion of the corrosion resistance the passive range can be used, where current density is independent of potential. It increases from iron, molybdenum to nickel. Chromium, which exhibits the widest passivation range (results not shown), could not be analyzed for dissolved products due to its excellent corrosion resistance resulting in concentrations below the LOD.

Compared to pure metals, the corrosion resistance increases for AISI 304 and especially for AISI 316 stainless steel. Voltammetric characteristics for both steels in physiological solution are consistent to those obtained in similar solutions [12–14]. The passivation of stainless steels is based on the formation of a duplex oxide layer consisting of an inner Cr_2O_3 layer and an outer Fe-oxide layer [11]. The composition of the layer is a function of the electrode potential and changes from Fe_3O_4 to Fe_2O_3 [11]. The outer layer contains incorporated oxides of minor elements, i.e. NiO in the case of AISI 304, and MoO_3 and NiO in the case of AISI 316 [11]. The beneficial effect of incorporation of molybdenum is reflected in the increase in the passive range by approximately 700 mV (Figs. 9 and 10).

The effects of various proteins differ for particular metals and alloys. In the presence of proteins stainless steel AISI 304 behaves similarly to pure iron. The following order of increase in the anodic current density and concentration of dissolved metal was observed: transferrin, fibrinogen, γ-globulin and albumin. The addition of these proteins results in the opposite order of increase in the case of nickel, molybdenum and stainless steel AISI 316: albumin, γ-globulin transferrin and fibrinogen.

Conclusion

The results of the present study indicate that proteins can have a significant effect on the passivation behavior of

individual metals and alloys. They can act as complexing agents for dissolved metal ions thus stimulating the dissolution rate of a base metal and, consequently, suppressing the formation of the protective oxide layer. When performing *in vitro* research of materials to be used in the human body, it should be taken into account that a pure saline solution does not entirely simulate the physiological situation. The effect of particular proteins differs on different metals and alloys. This result should be investigated further including determination of the stability constants of complexes formed between individual metal ions and various proteins.

References

1. T. M. E. SILVA, J. M. MONTEIRO, M. G. S. FERREIRA and J. M. VIEIRA, *Clin. Mater.* **12** (1993) 103.
2. K. MERRITT, S. A. BROWN and N. A. SHARKEY, *J. Biomed. Mater. Res.* **18** (1984) 1005.
3. P. KOVACS, in ''Corrosion '92, The NACE Annual Conference and Corrosion Show'' (Paper no. 214).
4. S. BROWN and K. MERRITT, *J. Biomed. Mater. Res.* **14** (1980) 173.
5. M. H. SAMITZ and S. A. KATZ, *Br. J. Dermatol.* **92** (1975) 287.
6. J. YANG and J. BLACK, *Biomaterials* **15** (1994) 262.
7. J. L. WOODMAN, J. BLACK and S. A. JIMINEZ, *J. Biomed. Mater. Res.* **18** (1984) 99.
8. G. C. F. CLARK and D. F. WILLIAMS, *ibid.* **16** (1982) 125.
9. A. MINOVIĆ, M.Sc. thesis, University of Ljubljana (2000).
10. M. POURBAIX, ''Atlas of Electrochemical Equilibria in Aqueous Solutions'' (NACE, Huston, Texas 1974).
11. I. MILOŠEV and H.-H. STREHBLOW *J. Biomed. Maters. Res.* **52** (2000) 404.
12. T. PIAO and S.-H, PARK, *J. Electrochem. Soc.* **144** (1997) 3371.
13. Y. OKAZAKI, T. TATEISHI and Y. ITO, *Mater. Trans. JIM* **38** (1997) 78.
14. J. PAN, C. KARLEN and C. ULFVIN, *J. Electrochem. Soc.* **147** (2000) 1021.

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