Available online at www.sciencedirect.com

SCIENCE DIRECT®

Acta Biomaterialia 2 (2006) 433–444

Acta BIOMATERIALIA

www.actamat-journals.com

Comparative corrosion study of “Ni-free” austenitic stainless steels in view of medical applications

L. Reclaru [a,*], R. Ziegenhagen [b], P.-Y. Eschler [a], A. Blatter [a], J. Lemaître [c]

[a] Corrosion and Biocompatibility Group, PX Holding S.A., R&D Dep. Blvd. des Eplatures 42, CH-2304 La Chaux-de-Fonds, Switzerland

[b] Cartier Horlogerie, Chemin des Aliziers, CH 2300 La Chaux-de-Fonds, Switzerland

[c] Swiss Federal Institute of Technology Lausanne, Surface Chemistry and Biomaterials Laboratory, MX-Ecublens, CH-1015 Lausanne, Switzerland

Received 16 November 2005; received in revised form 10 March 2006; accepted 13 March 2006

Abstract

The role of nickel in the biological response to alloys used in medical devices is of immense significance with regard to toxicology and biological performance. There is now a tendency to take nickel out of alloys for medical applications. However, this needs careful evaluation since no compromise is acceptable with regard to mechanical properties, corrosion resistance or any other harmful consequences due to the nickel substitution. This paper analyses the corrosion behaviour and cations released for five austenitic steels, nominally “nickel-free”. The analysis of electrochemical parameters, open circuit potential, polarisation resistance, Tafel slopes, corrosion current, breakdown potential, potentiodynamic polarisation curves, and coulometric analysis by zone, reveal that the new austenitic steels, nominally “nickel-free”, do not behave in the same way. In the family of steels studied, quite a large dispersion is noted in the corrosion behaviour. With regard to the crevice corrosion behaviour, the steel grades studied can be classified into three groups, with crevice potentials of 600–650 mV; 350–450 mV and 100–150 mV. The release of 18 cations (Al, Ba, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, P, Pb, Sn, Sr, Ti, and V) was studied by extraction tests in artificial sweat and bone plasma fluid. The extraction tests reveal that the “nickel-free” steels indeed release only faint traces of nickel. Yet many other elements, some of them potentially harmful, are released in significant amounts. Generally, the amount of cations released is substantially higher in the artificial sweat solution than in the bone plasma.

1. Introduction

Nickel-containing alloys are indispensable in a vast number of major applications. The importance of nickel as an alloying element will probably not diminish in the near future [1]. The role of nickel in biological responses to alloys used in medical devices is of major significance [2,3]. The toxicology and biological performance of nickel and nickel compounds have been the subject of numerous studies. There is evidence that high levels of nickel ions in tissues are the cause of genotoxic and mutagenic activity or in contact with the skin cause the most widespread contact allergy. It is still far from clear that nickel contained in alloys is responsible for all of these effects.

With respect to implantable devices, the evidence is much less clear because of the difficulty of establishing cause and effect in relation to the host response to implants within the tissue of the body. Up to the present, studies have tended to show that stainless steel endoprotheses are safe for revised hip arthroplasty, and that hypersensitivity to metals probably does not play a significant role in the loss of endoprostheses [4–7]. However, some authors recommend taking certain precautions when implanting into sensitive hosts [8]. There are authors that remind us the phenomena of corrosion and wear must be minimised [9] and others recommend the use of preventative tests such as lymphocyte transformation testing (LTT) [10].

With respect to consumer products in contact with the body, such items are not subject to medical device regulation, although the biological response is evident: in Europe, in the general population, 10–15% of adult females and

* Corresponding author. Tel.: +41 32 924 02 90; fax: +41 32 924 02 10.
E-mail address: lucien.reclaru@pxgroup.com (L. Reclaru).

1742-7061/$ - see front matter
doi:10.1016/j.actbio.2006.03.004

1–3% of adult males are allergic to nickel [11–13]. Teenagers and young adults tend to have a higher prevalence as body piercing is more common in this group [14]. Some experts believe that the prevalence of nickel allergy is increasing in adults, adolescents, and children in North America [15,16]. Thus for objects containing nickel intended for permanent contact with skin, the European Directive 94/27/EC imposes a ban on any objects, which exceed a rate of nickel release of 0.5 μg/cm^2 week Recently, a second Directive 2004/96/EC: "Piercing in the Human Body" has been issued which limits the rate of nickel release for this case to 0.2 μg/(cm^2 week).

Consequently, a certain number of steels containing nickel can no longer be used and it is believed that the limitations might get more stringent with future research. Furthermore, the nickel issue not only is a question of limitations and conformity, but a question of image for some brands. In this context, there is a strong tendency to replace CrNi-steels with a new generation of austenitic steels which do not have nickel as one of their constituents.

In addition to the ASTM standard F2229-02 designating a "Nitrogen Strengthened 23 Manganese-21-Chromium-1Molybdenum Low-Nickel Stainless Steel Alloy Bar and Wire for Surgical Implants", a number of other nominally "nickel-free" austenitic steels, stabilized with nitrogen and manganese, have appeared on the market. The development of these steels was driven particularly by the controversy on nickel allergies (i.e. in order to comply with the European Directives) as well as with respect to medical device applications.

The aim of this paper was to assess the corrosion behaviour of five of such new austenitic steels containing nickel only as a contaminant in negligible concentrations; and to compare them with conventional high quality nickel grades used in these applications. The corrosion phenomena studied are general corrosion, localised pitting corrosion, crevice corrosion and the analysis of the release of cations.

2. Materials and methods

The chemical compositions of the steels studied are shown in Table 1.

Table 1
Chemical composition in wt.% of the steels studied

Elements	#1	#2	#3	#4	#5	#6	#7
Cr	17.12	16.68	16	17.82	21.04	17.8	19.0–21.0
Mo	3.25	3.27	3.92	2.69	0.7	2.67	4.0–5.0
Si	1	0.49	1.09	0.156	0.26	<0.75	<0.70
Ni	0.026	0.02	0.11	0.25	0.02	13.1	24.0–26.0
Cu		0.02			0.01	<0.5	1.00–2.00
Mn	12.3	9.63	11.77	21.03	23.20	<2.00	<2.00
P	0.01	0.005	0.013	<0.01	<0.01	<0.025	<0.030
S	0.007	0.001	0.007	<.002	0.007	0.002	<0.015
N	0.89	0.55	0.85	0.68	0.99	<0.10	0.04–0.15
C	0.017	0.17	0.07	0.035	0.04	0.017	<0.02

In addition to the elements specified in the table, steel contains trace impurities which commonly include Co, V, Ti, Nb, Al, B and Ca.

Steel #1 was produced in an amount of several hundred kilos at the Swiss Federal Institute in Zurich [17]. Codes #2, #3, #4 and #5 steels were created by the iron and steel industry and are available on the market. In parallel, and by way of comparison, steel #6 was introduced (DIN 1.4441 or ASTM F138-97, often denoted as "316L medical grade"). Another steel, #7 (AISI 904L or DIN 1.4539) was also studied, although it is not a medical grade. Yet, it is currently used most commonly in applications in contact with skin, because it generally exhibits a higher corrosion resistance as compared to the AISI 316L grade due to the substantially higher Cr, Ni and Mo contents.

The characterisation of their corrosion behaviour was based on several analyses:

- Electrochemical evaluation of general corrosion by the rotating electrode technique.
- Evaluation of crevice corrosion and pitting corrosion.
- Evaluation of pitting and/or crevice corrosion in a solution of $FeCl_3$.

For the electrochemical tests specific to general corrosion, samples were in the form of 11 mm diameter cylinders spaced in ends made of Teflon. The samples used for crevice corrosion evaluation were 4 mm diameter rods spaced in sample holders made of Teflon adapted to the crevice testing technique in accordance with ASTM F746-87.

For evaluation tests of pitting resistance and crevice corrosion in a solution of $FeCl_3$, samples were in the form of 11 mm disks embedded in a resin.

The test surfaces were "mirror" polished with 0.1 μm diamond paste.

2.1. Corrosion evaluation by electrochemical techniques (ASTM G3-89 and ASTM G59-78)

The electrochemical measurements were made with a potentiostatic assembly of three electrodes: a working electrode (rotating electrode for general corrosion), a platinum counter-electrode and a reference electrode of saturated calomel (SCE). Given that diffusion phenomena play a very major role with regard to the changes which are produced at the metal/solution interface and consequently on the state and composition of the layers of the metal surfaces, readings were taken in a laminar system (criterion of $Re = 3200$) with a limit current $i_L = 56$ mA, and a rotational velocity at 300 rpm in order to control the mass transfer phenomena. The measurement system was managed by an EG& G Par 273A potentiostat modified with a baseline noise of 1 pA.

General corrosion was characterised by several electrochemical quantities:

- The open circuit potential (E_{oc}), recorded for 20 h with the sample immersed in a deaerated electrolyte with nitrogen.
- The polarisation resistance (R_p), calculated from traces of the polarisation curve at ±20 mV vs. E_{oc}.