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New generation super alloy candidates for medical applications: Corrosion behavior, cation release and biological evaluation

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ABSTRACT

Three super alloy candidates (X1 CrNiMoMnW 24-22-6-3-2 N, NiCr21 MoNbFe 8-3-5 AlTi, CoNiCr 35-20 Mo 10 BTi) for a prolonged contact with skin are evaluated in comparison with two reference austenitic stainless steels 316L and 904L. Several electrochemical parameters were measured and determined (E_{oc}, E_{corr}, i_{corr}, b_a, b_c, E_b, R_p, E_{crev} and coulometric analysis) in order to compare the corrosion behavior. The cation release evaluation and in vitro biological characterization also were performed.

In terms of corrosion, the results reveal that the 904L steels presented the best behavior followed by the super austenitic steel X1 CrNiMoMnW 24-22-6-3-2 N. For the other two super alloys (NiCr and CoNiCr types alloys) tested in different conditions (annealed, work hardened and work hardened + age hardened) it was found that their behavior to corrosion was weak and close to the other reference stainless steel, 316L. Regarding the extraction a mixture of cations in relatively high concentrations was noted and therefore a cocktail effect was not excluded. The results obtained in the biological assays WST-1 and TNF-alpha were in correlation with the corrosion and extraction evaluation.

1. Introduction

The biocompatibility is an important step for evaluation of the "in vivo" and "in vitro" interaction of a material in contact with a living tissue. In Europe since 2008 there is another vision concerning toxicology of chemicals for man, it is the REACH regulation (Registration, Evaluation, Authorisation and restriction of CHemicals) [1]. Thus the biocompatibility becomes a puzzle in the general picture of the evaluation of the effects of toxicity of chemicals which are in contact with us. The different chemicals originating from different sources, released at different moments and since different places could combine themselves to expose human beings to a cocktail of chemicals. Today one speaks of a burning scientific subject, the cocktail effect. European Chemical Agency (ECHA) [2] is trying to understand how the chemicals are released from different sources and how they combine with each other to give rise to a human exposure with adverse effects. A factor of complication is that the individual chemicals could become more dangerous only because of other chemicals with which they are mixed, the cocktail effect. For the moment there are no legal requirement imposing on the manufacturers to evaluate the combination of effects and risks of different chemicals due to a combined exposure. However, the modalities of such an evaluation are being examined by ECHA.

Also ECHA has developed a roadmap implementation plan on Substances of Very High Concern (SVHC) [3], that is, the Endocrine Disrupters (ED), substances which are carcinogens, mutagens or toxic to reproduction (CMR) and the sensitizers (skin sensitizers and respiratory sensitizers). It therefore means that in the near future we are obliged to reconsider our evaluation system of the toxicologies of the substances of the mixtures of substances and articles in man. Among the SVHC cited by ECHA, the substances that we find more frequently in contact with man are the skin sensitizer and respiratory sensitizer substances. Around 4000 substances are listed that can develop contact allergy. It is estimated that 15–20% of the population of Europe is made aware of at least one allergen. The allergic reactions to substances in products and articles, in both professional and private life, are a considerable and increasing health problem affecting major parts of the European population. The contact allergens, causing the dermatitis and the respiratory sensitizers, causing asthma and rhinitis.

This study is limited to metallic materials (steels and super alloys) supposed to be used in the manufacture of articles in prolonged contact

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with the skin [4,5]. They are steels, candidates for medical devices for watch straps. The watch straps are subjected to localized corrosion, especially by pitting and crevice in a sulfide–chloride medium, and to extensive wear in the articulations of the straps. The joint study in corrosion that is, the release of cations, of the cytotoxicity (ISO 10993-5) [6] and of immunotoxicity (TNF-α) (ISO 10993-20) [7], validates a choice of materials in accordance with the requirements of toxicologic and allergic security.

The external watch components are usually made in stainless steels of the X2 CrNiMo 18-13-3 grade (316L). This stainless steel is relatively soft (typically HV 200) and presents a good resistance to the generalized corrosion. On the other hand, it is a steel sensitive to the morphologies of corrosion by pitting and crevice.

Due to these reasons, three alloys were chosen and are part of this study:

- a super austenitic steel of the X1 CrNiMoMnW 24-22-6-3-2 N grade,
- a Ni Cr alloy, NiCr21 MoNbFe 8-3-5 AlTi grade,
- a CoNiCr alloy, CoNiCr 35-20 Mo 10 BTi grade.

These alloys present a high hardness (HV > 200), i.e. structurally either by age hardening and are very resistant to wear. They are strongly alloyed into oxidizing metals forming a strong passive layer. These alloys are used in strong aggressive media where they are also subjected to wear.

2. Materials and methods

2.1. Materials

According to the indications of the suppliers, the alloys are processed by vacuum melting and remelting. The compositions of the alloys studied are given in Table 1.

They are as follows:

- two austenitic stainless steels 316L (#1 — annealed condition) and 904L (#2 — annealed condition) taken as reference.
- a super austenitic steel, X1 CrNiMoMnW 24-22-6-3-2 N grade (#3 — annealed condition).
- a NiCr alloy, NiCr21 MoNbFe 8-3-5 AlTi grade (#4 — annealed condition, #5 — work hardened state 35%, #6 — work hardened state 35% + age hardened).
- a CoNiCr alloy, CoNiCr 35-20 Mo 10 BTi grade (#7 — work hardened state 35%, #8 — work hardened state 35% + age hardened).

The state of these alloys corresponds to their real usage for the manufacture of products.

Table 1
Chemical composition in % weight of the alloys tested. The compositions are given by the steel producers who have supplied these alloys to us.

	#1	#2	#3	#4, #5, #6	#7, #8
C	<0.03	<0.02	<0.03	<0.10	<0.025
Si	<1.00	<0.70	<1.00	<0.50	–
Mn	<2.00	<2.00	2.00–4.0	<0.50	<0.15
P	<0.045	<0.030	<0.035	<0.015	–
S	<0.015	<0.010	<0.020	<0.015	–
Al	–	–	–	<0.40	–
Ti	–	–	1.00–2.50	<0.40	<1.00
W	–	–	–	<0.40	–
N	–	–	1.50–2.50	–	<0.007
Cr	16.50–18.50	19.00–21.00	5.20–6.20	8.00–10.00	19.00–21.00
Mo	2.00–2.50	4.00–5.00	0.35–0.60	–	9.00–10.50
Ni	10.00–13.00	24.00–26.00	21.00–24.00	**Bal**	33.00–37.00
Co	–	–	–	–	**Bal**
Cu	–	1.20–2.00	–	–	–
Nb	–	–	–	3.15–4.15	–
Fe	**Bal**	**Bal**	**Bal**	20.00–23.	<1.00

The alloys studied are of industrial nuances developed by steel producers. The special alloys, #3, #4 and #7 are from materials controlled for place of origin and purity. The development of these alloys is carried out by a primary fusion under vacuum [VIM] and the casting of a remelting electrode. A secondary fusion of this electrode is carried out under vacuum [VAR] or under ESR in order to purify the alloy. The materials received do not undergo any remelting in the framework of this study. The objects from wrought materials are concerned and not the objects from castings. The control of homogeneity of alloys is carried out in production by steel producers on the materials received by metallography and by chemical analysis.

2.2. Metallographic characterization

The metallographical examinations and the chemical analysis are carried out by optical and scanning electron microscopy (Hitachi S-3400N with detectors of secondary electrons retrodiffused and EDX microprobe Thermo Scientific NSS).

2.3. Evaluation of the corrosion

The corrosion behavior of the alloys is carried out based on several techniques specific to morphologies of corrosion considered:

- electrochemical evaluation of the generalized corrosion by the technique of the rotating electrode and taking into account, for evaluation, the ASTM G3-89 [8] and ASTM G59-97 [9] standards,
- pitting and crevice corrosion according to the ASTM F746-87 [10] standard.

2.3.1. Evaluation of the general corrosion

The measurements are carried out on a potentiostat EG&G PAR273A with a cell of three electrodes adapted for the measurements with rotating electrode: reference electrode in saturated calomel (SCE) and the counter electrode in platinum.

The samples used are cylinders (Ø = 5 mm and L = 20 mm), polished (paper P600), washed under ultrasound (Tickopur® R30), and rinsed under deionized water (18 $M\Omega \cdot cm$) and in ethanol p.a. (Merck). The tests are carried out at the temperature of 37 ± 2 °C in an artificial sweat electrolytic solution according to EN 1811-2011 [11] with the following composition: $1 \pm 0.01\ g \cdot l^{-1}$ urea, $5 \pm 0.05\ g \cdot l^{-1}$ NaCl, $1 \pm 0.01\ g \cdot l^{-1}$ lactic acid, and $pH = 6.5 \pm 0.05$.

The electrochemical parameters measured and calculated are:

- the open circuit potential (E_{oc}) after 16 h of immersion in the deaerated electrolyte with Ar;
- the linear polarization resistance (Rp) in domain of Mansfeld, ±20 mV SCE vs. E_{oc},
- the Tafel slopes in the domain ±150 mV SCE vs. E_{oc},

Table 2
Test samples for the extractions and volume/surface ratio.

Sample	Area, S (cm^2)	Volume, V (ml)	V/S ratio (ml/cm^2)
#1	21.0	21.0	1.0
#2	13.5	22.0	1.6
#3 long	9.0	14.0	1.6
#3 transv	9.0	14.0	1.6
#4 long	8.8	8.8	1.0
#4 trans	6.0	7.0	1.2
#7 long	8.9	14.0	1.6
#7 transv	6.0	8.0	1.3