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Influence of the chemical composition and of the hardened state of four cast Ni-based and Co-based cast alloys on their behaviour in corrosion by an artificial saliva. Part 1: Case of the nickel alloy studied using stationary electrochemical techniques and EIS

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In one of the numerous medical fields, odontology is among the ones in which metallic alloys are often employed. Stainless steels are employed for arch wires in orthodontics, titanium alloys to fix individual teeth in jaw bone by surgical intervention, more or less noble metals (gold, platinum, palladium, silver...) in other applications of prosthetic dentistry. In the last example nickel-based alloys may replace noble alloys in the frameworks reinforcing mechanically fixed partial dentures. The association of nickel-based parent alloys sold together with primary and secondary solders, hidden by the artificial teeth the role of which is only aesthetic, allow the prosthesis resisting the bending solicitations during mastication. The use of nickel alloys started several decades ago [1], despite the biocompatibility [2] and allergy [3] problems which are often evoked about this element. They represent an interesting economic alternative since some of them may be simultaneously mechanically [4] and corrosion [5] resistant. However their elaboration and shaping may present some possibly problematic specificity (castability, chemical homogeneity, heat-treatments...). Nickel-based alloys as dental materials are present in the catalogue of various manufacturers besides traditional nobler alloys Au-based or Pt-based for example. Ivoclar Vivadent®, for instance, proposes the Pisces Plus (61.5Ni-22.0Cr-11.2W-2.3Al-2.6Si, all contents in wt.%) and the 4ALL (61.4Ni-25.7Cr-11.0Mo-1.5Si, in wt.%). Their base element is thus nickel and significant amounts in chromium are present to favour high corrosion resistance. Additional elements W or Mo, and Si or Al, also belong to their chemical composition: they are added to optimize their response to heat treatment and to improve their mechanical and corrosion resistances.

The mechanical properties of these alloys are of course of very high importance since this is in this field that they are used. But, knowing that, as the post-solder alloy, the extremities of the elemental parts of parent alloys are also possibly exposed to the buccal milieu, they must be themselves resistant against corrosion to be not at the origin of release of Ni²⁺ ions in mouth which can be dangerous for allergic patients. Since modifications can be brought to the alloys for their mechanical improvement, it is of great importance to better know the possible consequences of such changes for their corrosion resistance. This is the purpose of a latter work concerning the Pisces Plus alloy. Indeed, changing the chemical composition of the Pisces Plus alloy to study the effect of its microstructure and corrosion properties was earlier tested and the new properties investigated in a previous work [6].

In the present study this is the 4ALL alloy which will be subjected to chemical modification and to the study of the consequences on its corrosion properties. This will be explored by applying electrochemical methods to alloy electrodes immersed in a solution simulating saliva. Additionally, since hardening may result from mastication for the thinnest parts of the alloys, compression deformation will be applied to some parts and the possible influence on the corrosion behaviour will be specified by the same way.



Elaboration of the alloys and obtained microstructures

Two alloys, named NiMoCr and NiMoCrSi, simplified versions of the 4ALL alloy, were considered in this work. They were elaborated by foundry from parts of pure elements (Ni, Mo, Cr and Si, mainly from Alfa Aesar, >99.9 wt.%). These three to four elements were separately weighed to obtain charges of about 40 g. These ones were melted in order to generate the two wished alloys. Each charge was placed in the water-cooled crucible of a High Frequency Induction furnace (CELES). In the two cases the charge was isolated by a silica tube from the laboratory air. Three cycles (7 × 10⁻³ mbar – vacuum; incorporation of 600 mbars of pure Argon) were applied in the melting chamber. The final internal atmosphere was of about 300 mbars of pure Ar.

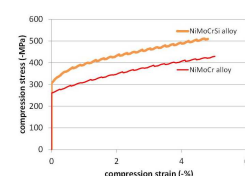
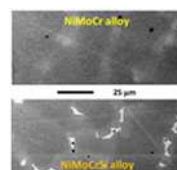
Melting and homogenization of the charge were realized by heating up to about 4kV and by respecting an isothermal stage of three minutes in the liquid state. Rather fast cooling led to solidification and solid state cooling.

The NiMoCr alloy seems to be single-phased but it is obviously not chemically homogeneous. As demonstrated by EDS measurements, the major part, dark grey is a little poorer in molybdenum (about 10 wt.%) and in chromium (about 25 wt.%) than the whole alloy (about 11 wt.% Mo and 26 wt.% Cr) while the minor pale areas are richer in molybdenum (about 17 wt.%) and in chromium (about 27 wt.%) than the whole alloy.

The as-cast NiMoCrSi alloy presents the same features (pale areas richer in Mo and dark areas poorer in Mo and Si, than the whole alloy) but with the additional presence of white particles, which are simultaneously richer in Mo and in Si than the whole alloy, twice the Mo and Si contents of the whole alloy's ones.

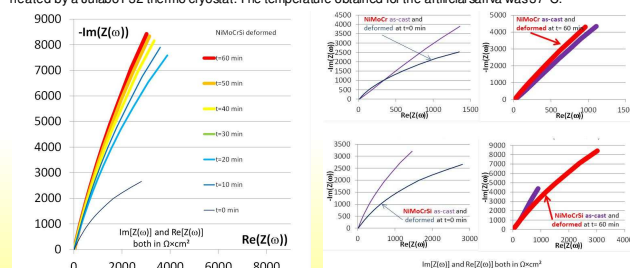
The two alloys were subjected to compression test until reaching almost 5% of total deformation. For the ternary NiMoCr, after an elastic deformation until about 260 MPa (yield strength) the applied stress was increased up to about 430 MPa in the plastic domain, with as result a longitudinal permanent deformation of about 6%. The Co alloy, the elastic deformation finished for about 310 MPa and the plastic one for about 510 MPa (resulting longitudinal permanent deformation: about 4%).

Parallelepiped parts (dimensions: about 6 mm × 6 mm × 4 mm) were machined in both ingots. Some of the parts were kept for the metallographic characterization in the as-cast condition and for the preparation of the "as-cast" working electrode. The others were subjected to compression deformation, leading to the "deformed" electrodes. The observations of the embedded and ground/polished as-cast alloys were done using a Scanning Electron Microscope (SEM) (manufacturer: JEOL, model: JSM 6010LA) which allowed observing them, mainly in Back Scattered Electrons (BSE) mode. The Energy Dispersive Spectrometer (EDS) attached to the SEM allowed semi-quantitative chemical analysis to control the obtained chemical composition. BSE observations and EDS measurements were done under a 20kV acceleration voltage. The parallelepipeds especially machined for that were subjected to compression test. Plastic deformation important enough was achieved to obtain a hardened version of the same alloys. For that one used an electrochemical testing machine (manufacturer: MTS Systems, model: Alliance RF150 model), of a 150kN capacity, equipped with auto-adjustable platens.



Electrochemical tests

The as-cast parts as well as the deformed ones were immersed in a liquid cold resin mixture but without submersion as for the ones devoted to constitute electrodes. After total stiffening the latter one was extracted from the plastic mould and placed in a vice. They were then sewed a little and the denuded part of an electrical wire was inserted by compression in the resulting slot. Thereafter they were incorporated again in the mould and additional liquid cold resin mixture was poured to totally immerse the upper part of the sample as well as the denuded copper of the electric wire. The metallic part of the obtained electrode was then ground until the 1200-grit paper, washed and dried. The obtained working electrodes were each associated to a platinum counter electrode and a Saturated Calomel Electrode (SCE), in a double-walled three-electrode cell containing a 9g/L NaOH aqueous solution simulating saliva (prepared from distilled water, the pH of which was, if necessary, adjusted to 7.4 by addition of either diluted HCl (for acidification) solution or diluted NaOH (for basicification) solution. The double-walled cell was maintained at 38°C by water circulation heated by a Julabo F32 thermo-cryostat. The temperature obtained for the artificial saliva was 37°C.



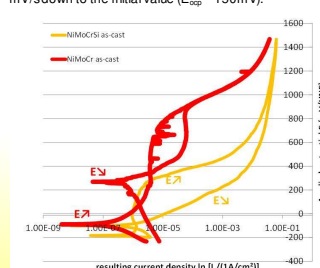
The six EIS results acquired for t=10, 20, 30, 40, 50 and 60 minutes after immersion of the deformed NiMoCrSi alloy, plotted according to the Nyquist representation

The EIS results were plotted according to the Nyquist representation ($-Z_{\text{im}}(\omega) = Z_{\text{im}}(\omega)$). Unfortunately the semi-circles were only partly obtained for the (1 Hz/100 kHz) frequency range. This problem, which is sometimes encountered with highly alloyed steels, suggests very high values of the transfer resistance. One can note that the obtained part of circle get more and more unbend when the immersion time increase (from 10 min to 60 min), suggesting that the transfer resistance goes on increasing. One can see that the EIS Nyquist curves tend to be significantly less unbend (lower transfer resistance) after plastic deformation than in the as-cast state, just after immersion as well as after one hour of immersion. Plastic deformation seems being detrimental for the corrosion behaviour of these two alloys.

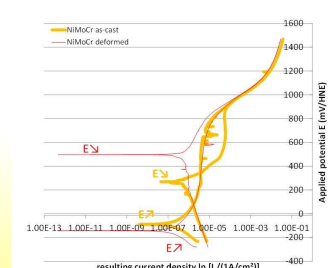
The first remark concerning the obtained polarization curves that can be done is the hysteresis shown by all of them. They all present a corrosion potential higher in the potential-decreasing part than in the potential-increasing part. A second remark is, for two of the three cyclic polarization curves, the higher values of anodic current density during the decrease in potential than during the previous increase in potential.

The presence of silicon in the NiMoCr base induces significant modifications in the microstructure (presence of particles particularly rich in Mo and Si) and in corrosion resistance. Globally its presence enhances three times the corrosion current in the active state. The contrary is however observed for the anodic current in the passive state. But the most important is that both alloys are very resistant against corrosion in this [9g/L NaCl; pH=7.4] solution often considered as valuable artificial saliva. Plastic deformation, possibly induced by mastication for the thinnest parts of metallic parts of dental prostheses, seems deteriorating this good behavior in corrosion, but certainly not in great proportions. One can conclude by saying that, for these two alloys, whatever their possible hardening, no significant release of ions, and thus corresponding induced allergy, is to be feared.

Two different apparatus were used for the electrochemical experiments for specifying the corrosion behaviour of the alloys. First, runs of Electrochemical Impedance Spectroscopy were performed using a Versastat potentiostat (Princeton Applied Research-EGG) equipped with an electronic card allowing EIS experiments. The test were driven, and thereafter exploited, using the Versastat software. The applied potential followed a sinusoidal variation around the corrosion potential (centred on E_{corr}), with an amplitude of 10 mV, for a frequency decreasing from 100,000 Hz down to 1 Hz. What was wished with these experiments: determining the transfer resistance R_t (corrected from the electrolyte resistance R_e) and the double-layer capacity C_d . The second used apparatus was an older potentiostat (model 263A) from Princeton Applied Research, driven by the M352 software of EGG/Princeton. The open circuit potential E_{oc} was first determined, then the working electrode was polarized at $E_{\text{oc}} - 150 \text{ mV}$. The applied potential increased thereafter until 1.225 V at 1 mV s⁻¹. After having reached the 1.225 V the potential decreased at -1 mV/s down to the initial value ($E_{\text{oc}} - 150 \text{ mV}$).



The cyclic polarization curves of the two alloys in their as-cast states



The cyclic polarization curves of the ternary alloy in its two states

The obtained values for β_c , which are rather scattered, are not in good accordance with the $\text{H}^+ + e \rightarrow \frac{1}{2} \text{H}_2$ cathodic reaction. The values of β_a are too high to be representative of the $\text{N} \rightarrow \text{N}^{2+} + 2e$ or $\text{Cr} \rightarrow \text{Cr}^{2+} + 2e$ or $\text{Cr}^{3+} + 3e$ anodic reactions. The values of the corrosion potential (E_{oc}) are higher for the NiMoCr alloy than for the NiMoCrSi one and the corrosion current density (i_{oc}) is three times lower for the ternary alloy than for the quaternary one. These two observations are consistent and they show that the NiMoCr alloy is more resistant against corrosion than the NiMoCrSi one. With a decrease in corrosion potential and a (very slight) increase in corrosion current density it seems that plastic deformation should deteriorates the corrosion resistance of the NiMoCr alloy. However, one can say that, in all cases, the corrosion current density is remarkably low, with values all $\leq 1 \mu\text{A/cm}^2$. Passivating is rather easy for both alloys, as-cast or plastically deformed. Furthermore reaching the passivation state seems easier for the silicon-containing alloy than for the ternary one (lower critical passivation current i_{c} and lower passivation potential $E_{\text{passivation}}$). Curiously the anodic current density seems higher when passivated than before overpassing the corrosion potential, except the NiMoCrSi as-cast for which the two current densities are equivalent. During the potential-decreasing phase a new corrosion potential appears, more or less higher than the one observed during the potential-increasing part.