Nickel release from 304 and 316 stainless steels in synthetic sweat. Comparison with nickel and nickel-plated metals. Consequences on allergic contact dermatitis

P. Haudrechy, J. Foussereau, B. Mantout and B. Baroux

Ugine Research Centre, 73400 Ugine, France

Service d’allergie, Clinique dermatologique, Hôpital Civil, Strasbourg, France

Abstract—Release of nickel from nickel or nickel-plated metals, is often responsible for allergic contact dermatitis. However, the effect of nickel-bearing stainless steels is not well known. In this paper AISI 304, 316 and 430 type stainless steels, as well as nickel and nickel-plated materials, are investigated. Three tests were carried out: electrochemical tests and leaching experiments in sodium chloride (0.05 M) and synthetic sweat solutions, and clinical patch tests on 50 patients already sensitive to nickel. Results of the leaching experiments show that nickel and nickel-plated samples release nickel in an amount much larger than 0.5 μg cm⁻² week⁻¹, in sodium chloride and synthetic sweat solutions of neutral or acidic pH (6.6 and 4.5 respectively), while AISI 304, 316L and 430 grades release nickel in very small amounts (<0.05 μg cm⁻² week⁻¹) in those solutions. These differences are attributed to the corrosion resistance of these stainless steels in chloride solutions, due to the protective effect of their chromium-rich passive films; for those materials, no localised corrosion is observed in the experimental solutions, even at pH 4.5, while pitting occurs on nickel and nickel-plated steel. However, complementary studies show that, for resulphurised stainless steels (for instance free-machining steels), the MnS inclusions may dissolve, mainly at acidic pH. In this case nickel release becomes larger. Thus, stainless steels AISI 304, 316 and 430, should not cause any allergic contact dermatitis. This was confirmed by the clinical patch tests which showed that 96% of the patients were intolerant to the nickel-plated samples, while low sulphur containing stainless steel samples elicited no reactions in the patients. Conversely, resulphurised stainless steel (AISI 303), led to reactions in 14% of the patients. In addition, it was shown that the dimethylglyoxime test was not relevant for selecting materials which cause no contact dermatitis. A new test was then proposed, in accordance with the present results.

INTRODUCTION

Release of Ni from nickel or Ni-plated metals, is often responsible for allergic contact dermatitis especially among women.¹⁻¹⁰ Ni bearing stainless steels are also said to be sometimes responsible for that kind of reaction.¹⁻⁶ However, while some data are available for the release of Ni from stainless steels through leaching experiments, no parallel investigations on the effect of their corrosion resistance was carried out.⁸ It is intended in this paper to investigate the behaviour of AISI 304, 316L and 430 grades, as well as of a resulphurised stainless steel (AISI 303), pure nickel and Ni-plated metal, with respect both to their corrosion resistance and Ni release in synthetic sweat or simpler chloride containing aqueous solutions.

The present study includes a parallel characterisation of the susceptibility of these various materials to induce a sensitisation to Ni and of their corrosion resistance, more precisely of their passivation ability in sodium chloride and synthetic sweat solutions of various pH. Measurements of Ni amounts released during leaching experiments in the same solutions, as well as clinical patch tests on nickel sensitive patients, are realised to compare the risk of sensitisation to Ni by the different
Finally the dimethylglyoxime spot test, which is commonly used to assess the "safety" of a material in regard to Ni allergy, is applied to the various metals studied here, in order to check its validity, which is very controversial.

EXPERIMENTAL METHOD

Experiments are conducted at the Ugine Research Centre except for the patch tests which are performed by J. Foussereau in the Strasbourg civil hospital.

Six materials are studied: pure nickel, nickel-plated steel, and four stainless steel grades for which the chemical analysis is given in Table 1. The stainless steel grades are AISI 304 and 316L as typical austenitic grades and additionally AISI 430 for comparison, since this ferritic grade does not contain nickel in a significant amount, from the viewpoint under consideration. Moreover, an AISI 303 grade, which is a resulphurised free machining austenitic stainless steel is considered. Experiments are performed either on polished surfaces (SiC paper, grade 1200) or on as-received surfaces (annealed and pickled for AISI 304, 316L and 430, and as machined for AISI 303). Prior to experiments, samples are cleaned ultrasonically in a solution of acetone + ethanol (50/50 in volume ratio). Four tests are carried out.

Potentiodynamic polarisation tests

These are conducted in 0.05 M sodium chloride solutions at pH 4.5 and 6.6 and in synthetic sweat solutions at pH 4.5, pH 4.5 was chosen according to a paper by Hemingway, as the lowest pH value found quoted in the literature for the physiological sweat. Composition of the synthetic sweat solution, is as follows: NaCl 0.3%, Na₂SO₄ 0.1%, urea 0.2% and lactic acid 0.2%. Tests are performed on circular samples (dia. = 30 mm except for AISI 303: dia. = 15 mm). The holder was designed in order to avoid any risk of crevice corrosion, which was verified all along the testing procedure.

Test solutions are maintained at 23°C and de-aerated with nitrogen + 3% hydrogen flux during 2 h prior to experiment and all along it. After 15 min at the rest potential, polarization curves are obtained from the rest potential to the pitting potential, using a 10 mV min⁻¹ scanning rate. Stainless steels are tested in the as-received condition and after polishing (followed by 24 h ageing in air), except in sodium chloride at pH 4.5 in which they are tested only in the as-received condition. Nickel-plated steel is tested as-received and Ni after polishing.

Leaching experiments

They are run mainly in the synthetic sweat solutions and in 0.05 M sodium chloride solutions at pH 4.5 at ambient temperature. Samples of the same grade, in the as-received condition, are immersed during one week in 100 ml of the solution naturally aerated (the total exposed area is given below in Table 2). Tests are also conducted in synthetic sweat solutions, at pH 6.6 for AISI 303, 304 and the nickel-plated materials.
nickel release from steels in synthetic sweat

Steel and at pH 3.0 with sodium chloride concentrations of 0.05 M and 0.1 M for AISI 304 and the nickel-plated steel, in order to study the influence of pH and chloride concentration on the leaching of Ni. After immersion, samples are rinsed with distilled water. The test solution is added with the rinsing solution, then analysed using Atomic Absorption Spectroscopy (detection limit = 10 µg L⁻¹), in order to determine the Ni concentration from which the leaching level (in µg cm⁻² week⁻¹) is deduced.

Dimethylglyoxime (DMG) spot tests

This test is based on the complexation of Ni ions with DMG to give a chromophoric compound. In ammoniacal solutions, Ni is complexed in the oxidation state +4, which develops a pink colouration. This colouration is characteristic of a positive reaction and thus supposedly reveals the presence of Ni. Thus it is commonly used by dermatologists to reveal the presence of Ni in alloys and so to determine if they can induce a Ni allergy in Ni-sensitive patients. However, that test does not seem to be very sensitive and relevant. For example, “false” negative reactions, due to an insufficient oxidation of Ni can appear. It is then recommended to etch the alloys with a strong acid like hydrochloric acid. This procedure leads to the metal dissolution in the active state and therefore reveals the presence or absence of nickel in the alloy composition. However, if the steel is used in the passive state (no corrosion), which is the normal situation if the steel is sufficiently resistant in the considered environment, its passive film forms a protection against the dissolution and then the test is probably not relevant. Moreover “false” positive reactions can occur because DMG is not a specific reagent for Ni. It also reacts with Fe. So it is necessary, for alloys containing Fe, to apply hydrogen peroxide which decolours the complexes of Fe but not those of Ni with DMG.

To verify the sensitivity and validity of that test, we applied it to the Ni-plated steel and to the four stainless steel grades, according to the method described in various papers. Tests are conducted on as-received samples in different ways:
- a few drops of NH₃ and of the DMG solution are placed successively or rubbed on the samples. Then a few drops of H₂O₂ are deposited to detect false positive reactions.
- to detect “false” negative reactions, samples can also be etched with 3 N HCl before applying NH₃ and DMG. Each grade of steels are tested three times.

Clinical patch tests

Those tests are performed on 50 Ni-sensitive patients, with circular samples of the four stainless steel grades and of the Ni-plated steel (1.5 cm in diameter) in the as-received condition. Prior to experiments, samples are washed with distilled water and cleaned with ethanol and then with ether. Tolerance is tested with Roc Neodermotest applied on the back and read after 48 and 72 h according to the international contact dermatitis research group recommendations.

EXPERIMENTAL RESULTS

Potentiodynamic polarisation

Curves obtained in de-aerated synthetic sweat solutions of pH 4.5 are shown on Fig. 1. Stainless steels and Ni-plated steel are in the as-received conditions while Ni is polished. A large domain of passivity is evidenced for the two austenitic grades, AISI 304 and 316L, and a small one for the ferritic grade (AISI 430), with a low passive current density (less than 1 µA cm⁻²) in each case. On the contrary, the resulphurised stainless steel does not present any passivity domain. The Ni-based materials present a peak of activity at about −225 mV(SCE) followed by a short passive domain characterised by a “high” current density (10 µA cm⁻² for Ni and around 200 µA cm⁻² for Ni-plated steel). From those results it follows that AISI 304 and 316L have a much higher passivation ability than the other materials in that solution.

In sodium chloride solution at pH 4.5, results are basically similar. For the AISI 304, 316L and 430, one observes a higher rest potential (ΔEₕ = 80 mV for AISI 304, ΔEₕ = 20 mV for AISI 316L and around 10 mV for AISI 430) and a lower pitting potential (ΔEₚ = 160 mV for AISI 304 and ΔEₚ = 90 mV for AISI 316L). Then, the
width of the passivity potential range is smaller than in synthetic sweat, but the passive current density, which varies as the cation release rate throughout the passive film, remains of the same order of magnitude. For the AISI 303 grade and the Ni-plated steel, there is no noticeable evolution. For pure Ni, the maximum anodic current density is significantly larger than in synthetic sweat (850 \mu A cm\(^{-2}\) instead of 50 \mu A cm\(^{-2}\)). Thus the chemical components added to the sodium chloride solution to form the synthetic sweat, seem to improve the corrosion resistance of some of the materials, which can be explained by an inhibitive effect.

- pH effect: acidification of the sodium chloride solution from pH 6.6 to 4.5 has the following consequences: (i) an increase in the rest potentials for all the metals, due to an increase of the redox potential of the solution. Thus for AISI 304, 316L and 430 grades, the passive domain is reduced and it disappears for AISI 303. (ii) An increase in the passive and in the active current density for the AISI 303 grade and the Ni based materials.

- A mechanical polishing decreases the rest potential with respect to the as received condition, in the neutral sodium chloride solution as well as in the acid synthetic sweat solution (in NaCl, \(\Delta E_{\text{rest}} = -130 \text{ mV}\) for AISI 304, \(-290 \text{ mV}\) for AISI 316L, \(-280 \text{ mV}\) for AISI 430 and \(-100 \text{ mV}\) for AISI 303. In synthetic sweat, \(\Delta E_{\text{rest}} = -630 \text{ mV}\) for AISI 304, \(-570 \text{ mV}\) for AISI 316L, \(-790 \text{ mV}\) for AISI 430 and \(-70 \text{ mV}\) for AISI 303), while the pitting potentials seem fairly unchanged. It results in a larger passive domain, but the corresponding passive current density is higher.

**Leaching experiments**

Results obtained for the tests run in synthetic sweat solutions are shown on
Nickel release from steels in synthetic sweat

Fig. 2. They are averaged over several tests the number of which is given in parenthesis. \((\text{Ni})_{\text{Re}}\) is the Ni quantity leached in the test solution by the metallic samples during the 1-week experiment. For each type of solution a blank is also analysed by atomic absorption spectroscopy and when traces are found, the necessary corrections are made on the results obtained for the test solutions.

It appears from those results that leaching levels of Ni from Ni or Ni-plated steel is very high, of the order of 100 \(\mu\)g cm\(^{-2}\) week\(^{-1}\), while it is much lower for the low sulphur containing stainless steels studied here: around 0.1 \(\mu\)g cm\(^{-2}\) week\(^{-1}\) in the most corrosive solutions and often beyond the detection limit of 0.014 \(\mu\)g cm\(^{-2}\) week\(^{-1}\) (for AISI 304, 316L and 430). On the other hand the AISI 303 grade exhibits a higher \((\text{Ni})_{\text{Re}}\) value than the other stainless steels but well below those observed on pure nickel and Ni-plated steel. The nickel release is close to the value of 0.5 \(\mu\)g cm\(^{-2}\) week\(^{-1}\), which is currently considered as being a sensitisation limit, below which a weak reactivity on Ni sensitive patients is expected.

In 0.05 M NaCl solution of pH 4.5, \((\text{Ni})_{\text{Re}}\) values for stainless steels are similar to those obtained in synthetic sweat solutions of pH 4.5 while the Ni-plated steel shows a lower \((\text{Ni})_{\text{Re}}\) value in NaCl (=20 \(\mu\)g cm\(^{-2}\) week\(^{-1}\)) but still higher than the above limit.

In synthetic sweat of pH 3.0 with a 0.1 M NaCl concentration, results are similar for the Ni-plated steel, while \((\text{Ni})_{\text{Re}}\) is slightly higher for the AISI 304 grade (0.1 \(\mu\)g cm\(^{-2}\) week\(^{-1}\)).

So pH and chloride concentration have no noticeable influences on Ni release for Ni-plated steel, which is due to the low corrosion resistance of that material in each of the leaching solutions used. On the other hand, one observes an increase in the Ni release from stainless steels, when the corrosivity of the leaching solution increases.

So, release of Ni is qualitatively well connected to the corrosion resistance (more precisely the passivation ability) of the alloys. However, it is difficult to relate quantitatively the Ni release and the anodic current measured in electrochemical
tests, since this Ni release rate probably decreases with time during the leaching experiment.

**Dimethylglyoxime test**

The DMG test applied to the Ni-plated metal samples without the acid etching is always positive. A pink colouration appears and remains when we apply $\text{H}_2\text{O}_2$. Applied to the stainless steels, the test is negative: without acid etching, no colouration appears; with an acid etching with $\text{HCl}$, a pink colouration occurs on each sample, but disappears with $\text{H}_2\text{O}_2$. It shows then, that the colouration was due to the complexation of Fe with DMG and not of Ni with DMG.

The obtained results show that this test does not differentiate the various stainless steels studied here, while they do not release Ni in the same amount: according to that test the AISI 303 grade would not elicit Ni sensitisation, while its Ni release measured in leaching experiments is around the sensitisation limit. Moreover to detect false negative reactions, it is recommended to etch the samples with a strong acid. For a stainless steel, such an attack results in the destruction of the passive film and in the loss of its corrosion resistance. Thus, the test is then applied on the bulk of the alloy but no more on the surface, which is in contact with the skin.

The irrelevance of that test led us to propose another test which would differentiate between stainless steels, that is to say stainless steels susceptible to release a low or a high quantity of metallic elements including Ni. Since among austenitic stainless steels, sulphur content is the main parameter which exerts an influence on the corrosion resistance, we applied a very simple test with nitric acid which reveals the presence of sulphur. We used a solution of 3 N nitric acid and applied a drop of it on each stainless steel grade for 5 min. The AISI 304, 316L and 430 grades showed no reaction, while on the AISI 303 samples, a black colouration appeared which indicated the presence of a high quantity of sulphur.

**Clinical patch tests**

Results of the patch tests are presented on the histogram of Fig. 3.
It clearly reveals that the low sulphur stainless steels studied here, including austenitic stainless steels, elicit no allergic reactions in Ni-sensitive patients. On the contrary, 96% of the patients are intolerant to Ni-plated metal and 14% to the resulphurised austenitic stainless steel (AISI 303), which has the lowest corrosion resistance, among stainless steels, as previously seen.

**CONCLUDING REMARKS**

The nickel amount which can be released in a corrosive environment is proportional to the anodic current density, which corresponds to the cationic current flowing from the metal to the corrosive solution. This current density, $i$, depends on the rest potential, $E_{\text{rest}}$, which is itself determined by the cathodic reaction which is effective at the metal–solution interface. In aerated neutral media, this cathodic reaction is the oxygen evolution one which roughly determines the rest potential. This remains true at lower pH (such as pH 4.5), when the rest potential is not controlled by the hydrogen evolution reaction. Then, studying the current density $i(E)$ versus electrode potential $E$ in de-aerated media, allows an estimate of the current density in aerated media as being roughly $i(E_{\text{rest}})$. In this study, no estimation of the corrosion current was made using for instance impedance techniques or Tafel slope methods, since the normal situation for the problem under consideration is to use passive materials. Nevertheless, the polarisation curves in de-aerated media allow a qualitative comparison of the cation release tendency of the various materials, taking into consideration both the width of the passivity region and the level of the anodic current in this passivity region.

From this viewpoint, the polarisation curves obtained in various chloride solutions (synthetic sweat of pH = 4.5 and NaCl of pH = 4.5 and 6.6), show a much better behaviour of the stainless steels 304, 316L and 430 grades compared to pure nickel or Ni-plated metal. This can be attributed to the stability of the passivation of stainless steels in those solutions, while Ni passivity is clearly destroyed in such conditions.

Then, using stainless steels in some conditions where the passive film remains stable, should not lead to any risk of contact dermatitis.

The case of the resulphurised grade AISI 303 must be considered in a different way. It is well known that manganese sulphide inclusions, while very favourable for free machinability, are very detrimental for the corrosion resistance. This work shows that the corrosion resistance of AISI 303 is not sufficient in the considered solutions for avoiding any risk of contact dermatitis, even if the risk is much lower than for Ni-plated steels. Thus, the use of Ni containing stainless steels for prolonged contact with the skin should be restricted to low sulphur containing stainless steels (typically less than 0.03%, while AISI 303 contains of the order of 0.3%). The nitric acid spot test that we proposed in this paper allows separation of the two types of steels.

Conversely, the DMG spot test appears irrelevant to determine which alloys can induce nickel intolerance because it includes an acid etching. As a matter of fact, in the case of stainless steels, that attack destroys their passive film and so greatly reduces their corrosion resistance, a fundamental property which enables them to be safe in regard to nickel allergy. To be valid, the test must be applied to the surface that really contacts the skin and not to the bulk of the alloys. Thus, instead of that test, it seems more appropriate to apply a test which is able to differentiate stainless steels in regard to their corrosion resistance, such as the nitric acid spot test.
Clinical tests and leaching experiments confirm these conclusions. Results of the patch tests showed that no allergic reactions occurred with low sulphur stainless steels, while some of the patients (14%) reacted to the AISI 303 grade and most of them were intolerant to the Ni-plated metal (96%). It is also of interest to compare the Ni release value in synthetic sweat solution to the sensitisation limit of 0.5 µg cm$^{-2}$ week$^{-1}$. According to that limit, the low sulphur stainless steels would elicit no reactions in Ni-sensitive patients, while the AISI 303 grade would provoke reactions only in patients with an acid sweat, since in the acid leaching solution (pH = 4.5), we found a (Ni)$_{Re}$ value of 1.4 µg cm$^{-2}$ week$^{-1}$, but at pH = 6.6 it is inferior to 0.5 µg cm$^{-2}$ week$^{-1}$ (0.3 µg cm$^{-2}$ week$^{-1}$). Finally the Ni-plated steel, as well as pure nickel, would elicit strong reactions in the majority of the patients. Patch test results assess these assumptions and so validate the value of 0.5 µg cm$^{-2}$ week$^{-1}$ as a sensitisation limit.

So, a good correlation appears between the corrosion resistance in neutral or slightly acid sodium chloride solutions, the Ni release levels in the same solutions and the probability that the used material elicit nickel allergic reactions in Ni-sensitive patients. The main conclusion is that the AISI 304, 316 and 430 grades can be used without any problem for prolonged contact with skin, while Ni-plated metals and, a fortiori pure nickel, must be prohibited. Finally, the use of an appropriate nitric acid spot test allows to select the convenient low sulphur containing stainless steels while the dimethylglyoxime test is irrelevant for this purpose.

REFERENCES