Nickel release: the unexpected behavior of electroplated stainless steel

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Introduction

Steel is one of the most important materials in the world because, besides being relatively inexpensive, it can be continuously recycled without losing its technical properties. Nevertheless, its presence in the electroplating sector is very limited due to the difficulties involved in electroplating. Stainless steel (316L) contains approximately 10.5% chromium, which forms a surface oxide layer that passivates the steel [1], making it resistant to corrosion and difficult to electroplate. The main method of electroplating stainless steel is generally through the deposition of nickel, but a strict regulation limits its use due to the issues related to this metal. Indeed, nickel allergy is the most frequent contact allergy in the world, affecting 10–15% of women and a few % of men in the general population [2]. Therefore, the European Community has recently banned items whose nickel release is greater than 0.5 µg/cm² · week (UNI EN 1811: 2011).

Even when nickel-free processes are used, it is possible that steel objects release nickel beyond the threshold value allowed by current legislation. This is because the steel itself contains nickel (ca. 12% in 316L), so the removal of the surface oxide layer during the electroplating process may facilitate the release of nickel.

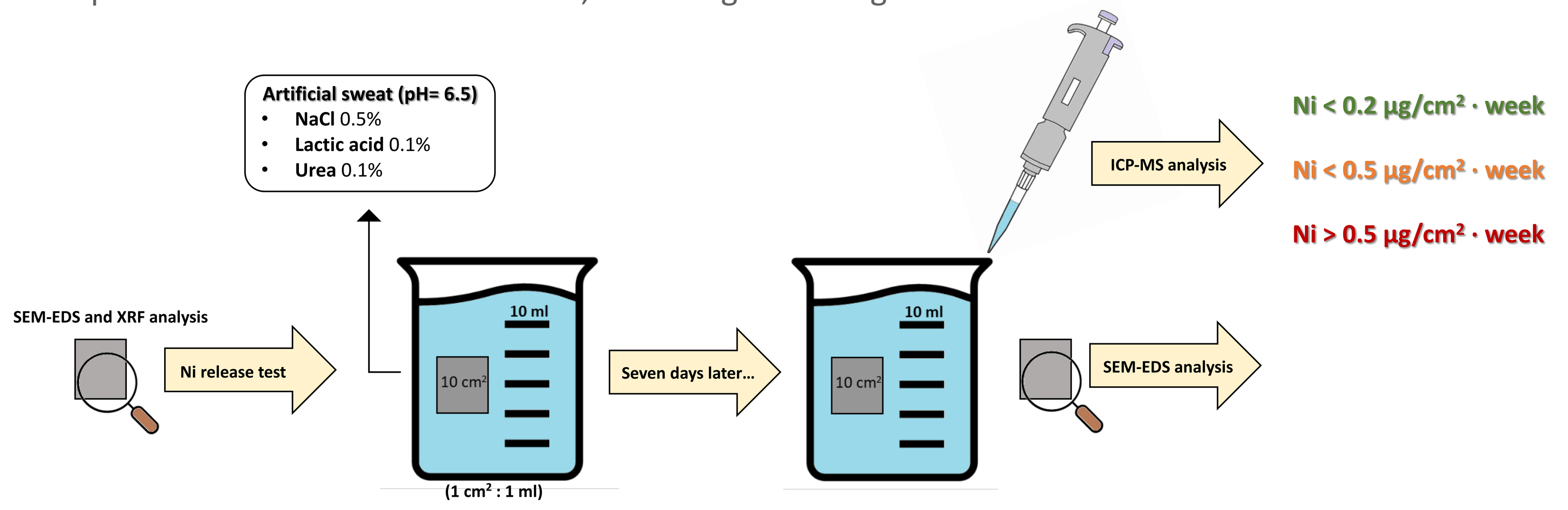
In this study, we evaluated the nickel release from stainless steel 316L after each galvanization step, starting from surface activation until electroplating processes.

Materials and Method

The leading actor is stainless steel 316L, as it is and after different treatments, galvanic and otherwise.

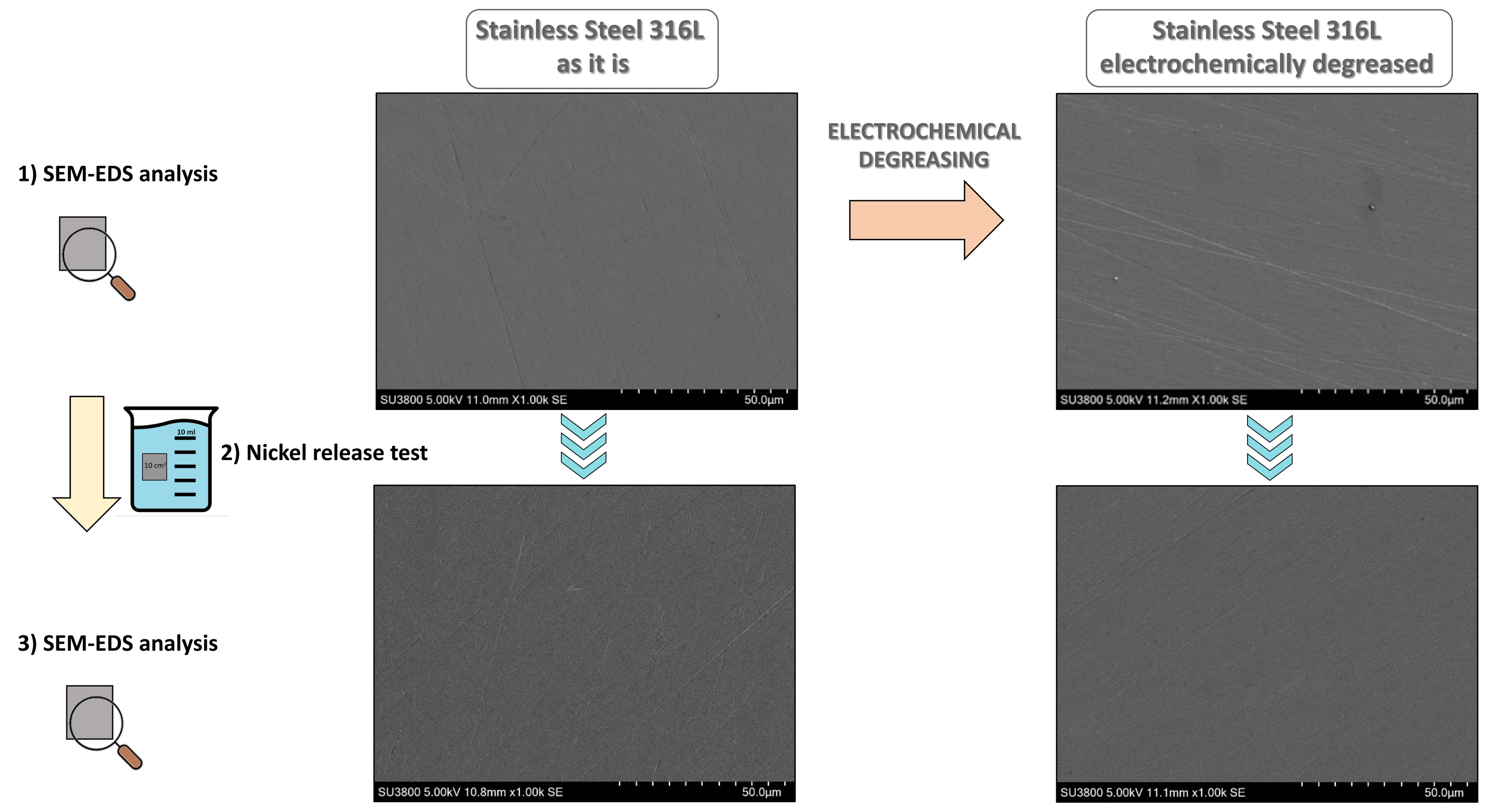
Morphology, composition and thicknesses were investigated, using respectively Scanning Electron Microscopy - Energy Dispersive X-Ray Spectroscopy (SEM-EDS) and X-ray Fluorescence Spectroscopy (XRF).

All samples were tested for nickel release, according to the regulation UNI EN 1811: 2011.



Experimental results

- **PRE-GALVANIZATION TREATMENTS**



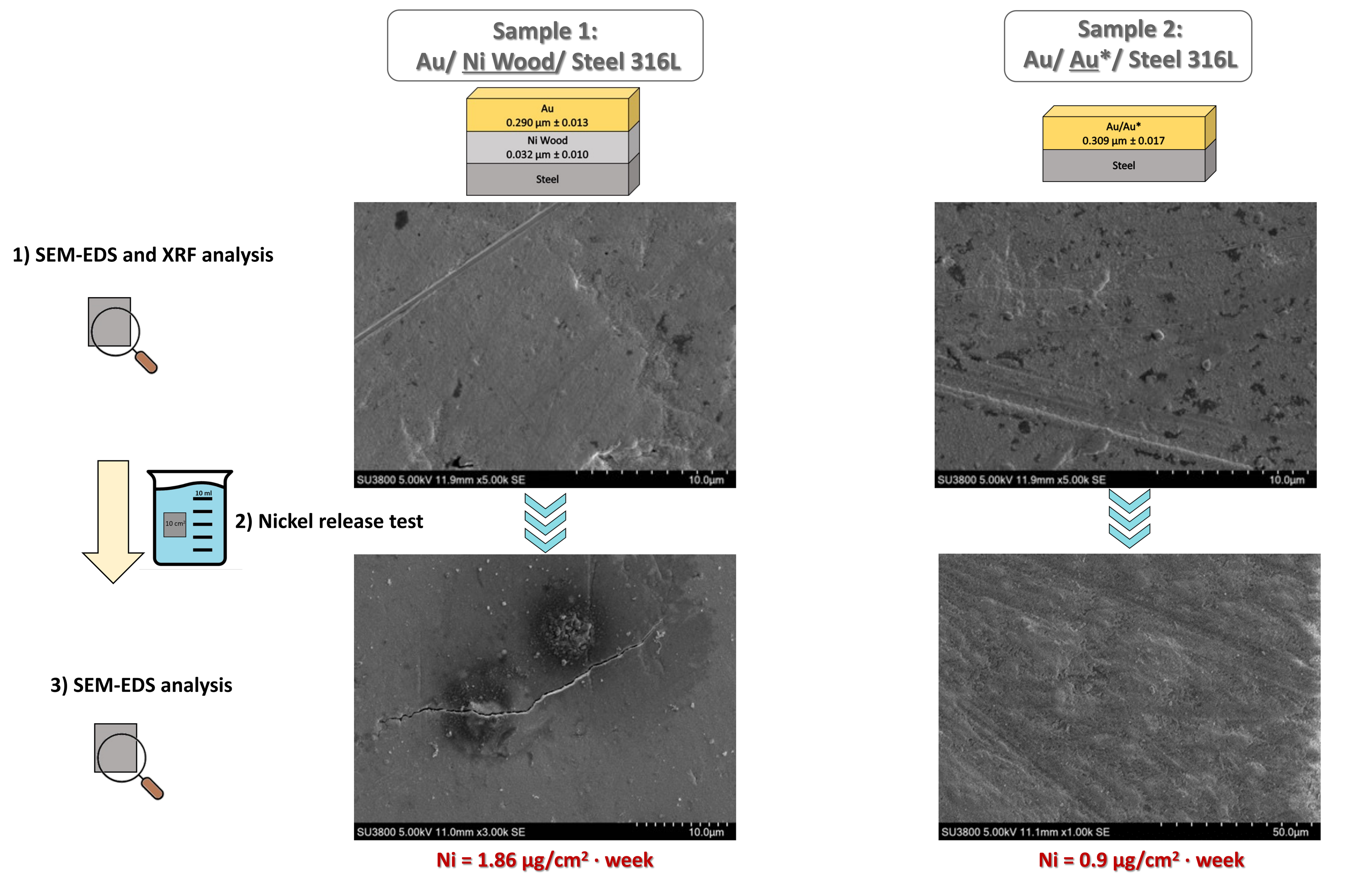
Is now well known that **stainless steel 316L, as it is**, does not release nickel (Ni < 0.03 µg µg/cm2 · week in sodium chloride 0.05 M and in synthetic sweat solutions [3]).

We evaluated the **electrochemical degreasing** process, required for a proper electroplating, investigating three different potentials (low, medium and high), reported in terms of current density:

1 A/dm², 20 A/dm² and 100 A/dm². We also evaluated the role of neutralization with H_2SO_4 5% after electrochemical degreasing process , then two sets of samples were tested for each chosen potentials.

We proved that electrochemical degreasing do not lead to an increase in the nickel release, indeed, the values of Ni obtained from ICP-MS analysis, for all these samples, is **< 0.2 µg/cm² · week**.

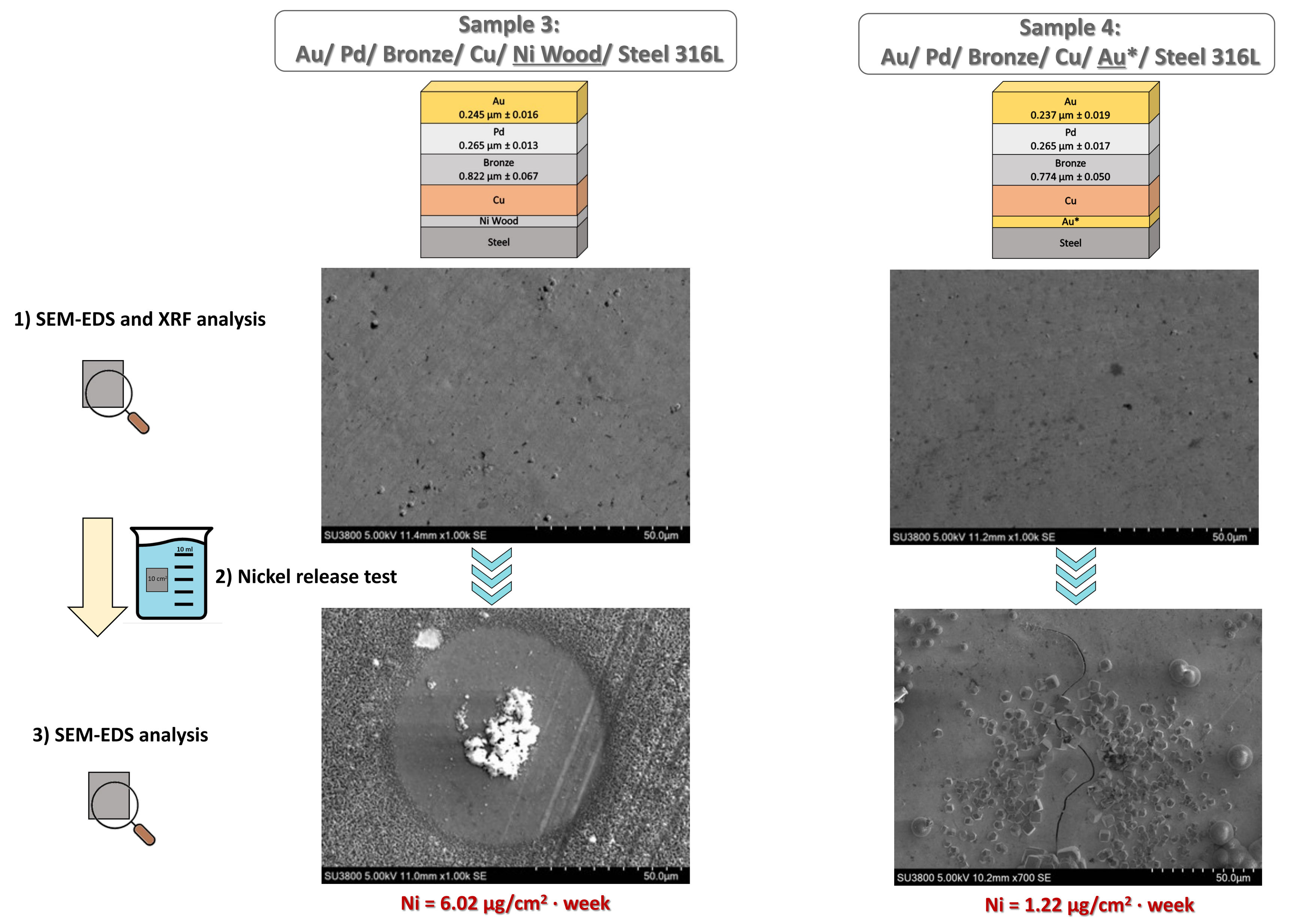
- **ELECTROPLATING PROCESSES**



We performed a new Ni-free process (Au*) for electroplating gold directly on stainless steel 316L (**sample 2**).

Thanks to this innovative galvanic cycle, is possible to halve the quantity of nickel released, passing from 1.86 to 0.9 µg/cm² · week.

- **FULL GALVANIC CYCLES**



It is clear to see that Ni release is related to the poor adhesion of galvanic deposit on stainless steel 316L. Indeed, SEM-EDS analysis show many cracks in the galvanic coatings; electrodeposited copper comes out from the latter, spreading on the sample's surface.

Our innovative Au* layer shows a better adhesion, since the released Ni value drops from 6.02 µg/cm² · week for traditional Ni-based galvanic cycle, to 1.22 µg/cm² · week for our Ni-free process.

Being able to reduce nickel release by 5 times is already a great achievement; further studies will be necessary to optimize the electroplating process directly on stainless steel 316L, improving adhesion feature.

SUMMARY

We assessed that stainless steel 316L, **as it is** and **electrochemical degreased** releases nickel below the threshold value allowed by current legislation **< 0.2 µg/cm² · week**.

Conversely, when a traditional nickel-based electroplating process is performed, stainless steel 316L (**sample 1**) fails the nickel release test (**Ni = 1.86 µg/cm² · week**). By electroplating gold directly on stainless steel 316L (**sample 2**) with our innovative Ni-free galvanic bath, is possible to halve the quantity of nickel released, passing from 1.86 µg/cm² · week to **0.9 µg/cm2 · week**.

The results obtained are promising even in the case of full galvanic cycle. Samples electroplated with traditionally Ni-based cycle (**sample 3**) release Ni^{2+} five times more than those with our innovative Ni-free cycle (**sample 4**). Indeed, Ni^{2+} release value obtained for Ni-based cycle is **6.02 µg/cm² · week**, while for our Au-based cycle is **1.22 µg/cm² · week**.

We guess that Ni release from electroplated steel is related to poor coating adhesion.

Indeed, sample's surface show many cracks in the galvanic coatings; electrodeposited copper comes out from the latter, spreading on the sample's surface! However, our innovative Au* layer shows better adhesion than traditionally Ni Wood. Further study will be necessary to optimize the electroplating process directly on stainless steel 316L, improving adhesion feature and, consequently, minimizing nickel release problem.

References

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