The unexpected behavior of electroplated steel towards the release of Nickel

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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.

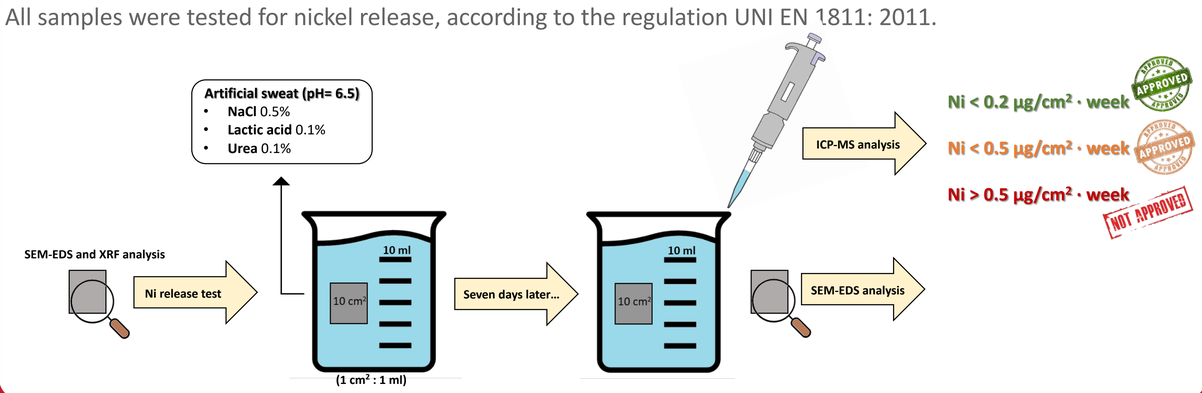
In this study, we evaluated the nickel release from stainless steel 316L after each galvanization step, starting from surface activation until electroplating processes.

Materials and Method

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

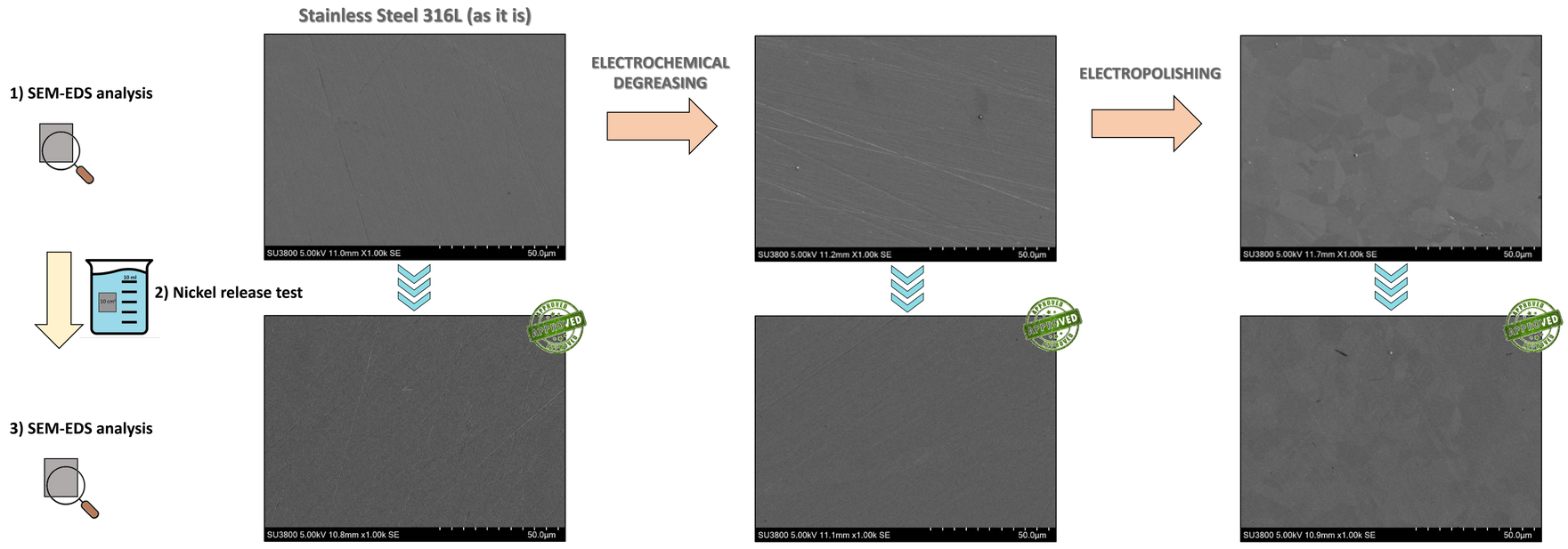
Morphology, composition and thicknesses were investigated, using respectively Scanning Electron Microscopy - Energy Dispersive X-Ray Spectroscopy (SEM-EDS) and X-ray Fluorescence Spectroscopy (XRF).

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 proved that the surface activation steps, required for a proper electroplating process (**electrochemical degreasing** and **electropolishing**), 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**

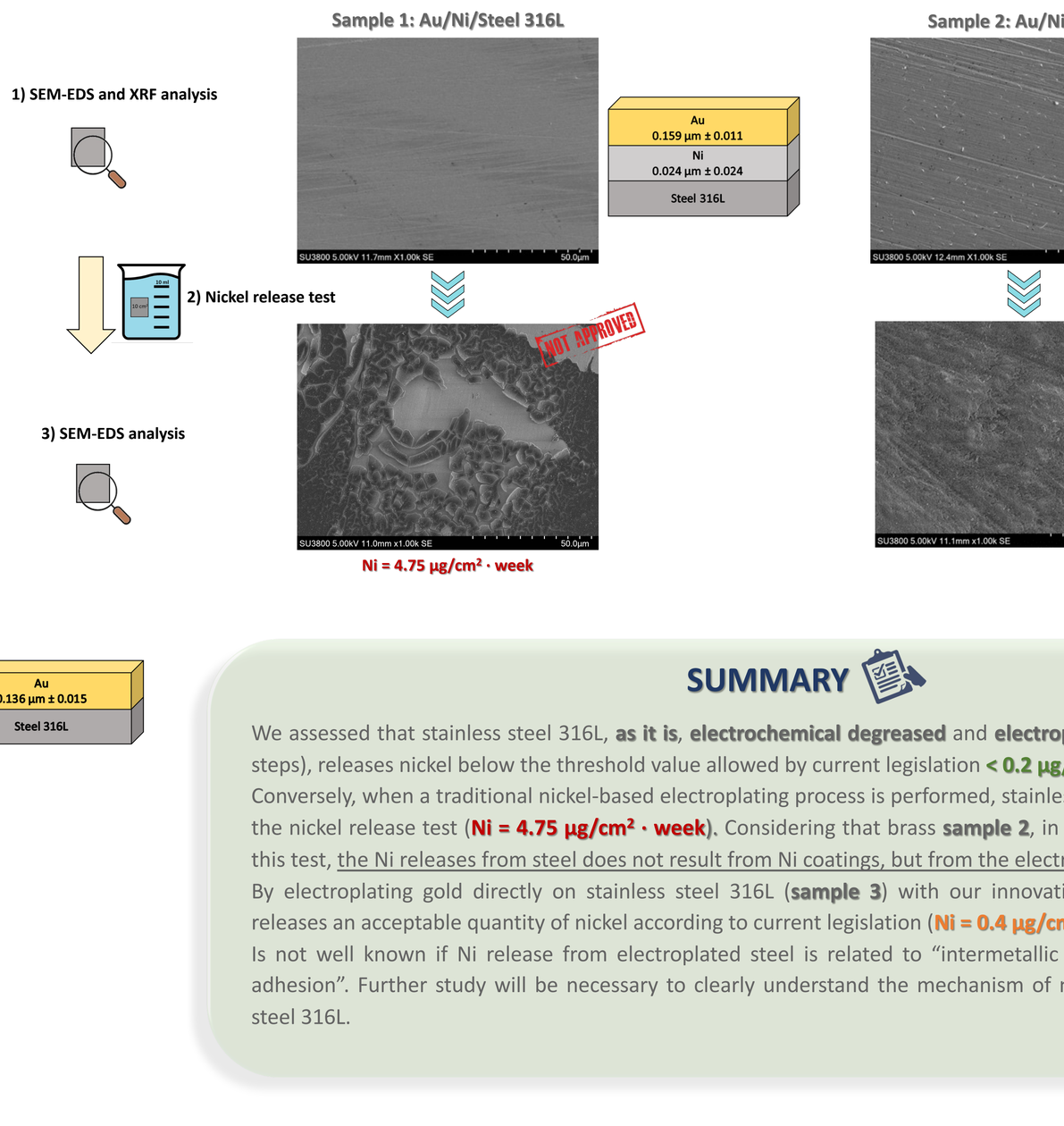
Despite the same electroplating process (Ni and Au) was used for both **samples 1** and **2**, only the steel one releases nickel beyond the threshold value allowed by current legislation (**Ni = 4.75 µg/cm² · week**).

Based on this comparison, the high release of nickel from stainless steel 316L does not result from Ni coatings, but from the electroplating process!!

We performed a new Ni-free process (**sample 3**) for electroplating gold directly of on stainless steel 316L.

Thanks to this innovative galvanic cycle, stainless steel 316L releases an acceptable quantity of nickel according to current legislation (**Ni = 0.4 µg/cm² · week**).

Also, the corrosion resistance is significantly improved compared to the samples with the traditional nickel-based galvanic cycle.



SUMMARY

We assessed that stainless steel 316L, **as it is**, **electrochemical degreased** and **electropolished** (surface activation steps), 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 = 4.75 µg/cm² · week**). Considering that brass **sample 2**, in equal conditions, overcome this test, the Ni releases from steel does not result from Ni coatings, but from the electroplating process!

By electroplating gold directly on stainless steel 316L (**sample 3**) with our innovative Ni-free galvanic bath, it releases an acceptable quantity of nickel according to current legislation (**Ni = 0.4 µg/cm² · week**).

Is not well known if Ni release from electroplated steel is related to “intermetallic diffusion” or “poor coating adhesion”. Further study will be necessary to clearly understand the mechanism of nickel release from stainless steel 316L.

References

[1] C. O. A. Olsson, D. Landolt, Electrochim. Acta. 48 (2003) 1093-1104.
[2] C. Cavellier, J. Foussereau and M. Massin, Contact Dermatitis 12 (1985) 65-75.
[3] P. Haudrechy, J. Foussereau, B. MANTOUT and B. Baroux, Corrosion Science 35 (1993) 329-336.

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