



## Research article

# Nickel release from 316L stainless steel following a Ni-free electroplating cycle

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## ARTICLE INFO

## Keywords:

Nickel release  
Electroplating  
316L  
EN 1811  
Dermatitis  
Nickel allergy

## ABSTRACT

Electroplating can induce nickel release even from 316L stainless steel, typically considered safe. In this work, the influence of different electroplating processes and surface treatments on nickel release was evaluated. The nickel release was tested according to the EN 1811 standard. The impact of surface roughness on nickel release was assessed by comparing polished and unpolished samples. Results indicate that internal stresses can worsen nickel release, while increasing the thickness of the precious metal layer is beneficial. To corroborate our hypothesis, it was verified that coatings obtained through physical vapor deposition (PVD), without removing the passivation layer of the steel, did not release nickel. For these reasons, we identified the main cause of nickel release as the combined effect of the removal of the passivation layer of stainless steel and the microporosity of the electroplating process.

## 1. Introduction

Steel is one of the most important materials globally because, besides being inexpensive, it can be continuously recycled without losing its technical properties. Stainless steel (SS) is a type of steel containing a minimum of 10.5 % chromium (Cr) and a maximum of 1.2 % carbon [1]. It earns the adjective “stainless” due to its ability to be passivated in the air or oxidizing environments, forming a thin, compact oxide layer that shields the bulk material. The chromium oxide film formed superficially, typically about 1–3 nm thick, provides passivation to the alloy, giving it resistance to corrosion and metal release [2]. To ensure homogeneous coverage of the protective film on the entire surface, the percentage of chromium in the alloy must be more than 10 % [3]. Thanks to its unique properties, such as good resistance to corrosion and creep at high temperatures, stainless steel is widely used as a structural material in chemical, petrochemical, power engineering, as well as in the vehicle and aviation industries [4].

AISI 316L SS is a low-carbon version of AISI 316 stainless steel, with the main components being approximately 65 % iron, 10–14 % nickel (Ni), and 16–18 % chromium. 316L SS is extensively used in many applications due to its superior corrosion resistance,

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<https://doi.org/10.1016/j.heliyon.2024.e37125>

Received 29 March 2024; Received in revised form 23 August 2024; Accepted 28 August 2024

Available online 29 August 2024

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smoothness, biocompatibility, and cleanability after electropolishing treatments [5]. It finds applications in various fields, from the construction industry [6] to medical applications, such as the fabrication of implantable devices [7]. However, its presence in the electroplating sector is limited due to difficulties involved in electroplating. The chromium content (16–18 %) is responsible for the formation of a surface oxide layer that passivates the steel, making it resistant to corrosion and challenging to electroplate. The primary method of electroplating SS involves depositing a thin adhesion layer of nickel, typically using Wood's nickel strike formulation. This formulation contains 240 g/L of nickel chloride and 125 mL/L of concentrated HCl. It operates at room temperature, and the deposition is typically performed by providing 6 A/dm<sup>2</sup> for 30 s [8]. This bath can activate and ensure good adhesion when the substrate is stainless steel, nickel alloy, or other metals that form an oxide layer inhibiting material adhesion [9].

The presence of nickel in 316L SS may raise concerns about the release of nickel ions, which are connected to allergic sensitization and reactions. Nickel allergy is the most frequent contact allergy globally, affecting 10–15 % of women and a few percentage of men [10,11], leading to dermatitis [12,13]. Therefore, strict regulations limit its use due to issues related to this metal. The European Community has recently banned items whose nickel release exceeds the amount defined by the EN 1811:2023 standard, the reference method for the release of nickel for articles pierced in the human body or that come into direct and prolonged contact with the skin. The nickel limits imposed by the regulation EN 1811:2023 are 0.2 µg/cm<sup>2</sup>/week for post assemblies inserted into pierced ears and other pierced parts of the human body, and 0.5 µg/cm<sup>2</sup>/week for other products intended for direct and prolonged contact with the skin.

Although SS could experience corrosion in a high saline environment [14–17], it has been proven that 316L SS does not release nickel more than 0.2 µg/cm<sup>2</sup>/week [18], and with its use, no severe cases of dermatitis have been reported [19]. Therefore, it is considered suitable for use in articles in direct and prolonged contact with the skin. Unexpectedly, 316L SS items undergoing the electroplating process may raise concerns about the release of nickel ions, even when nickel-free electroplating processes are used. In fact, electroplated steel objects might release nickel beyond the threshold value allowed by current legislation. This is because the steel itself contains nickel (approximately 12 % in 316L), so the removal of the outermost oxide layer during the electroplating process may facilitate nickel release. In this study, we evaluated the nickel release from 316L stainless steel after each electrochemical step, starting from surface activation until electroplating processes. The aim of this work is to understand the mechanism behind this phenomenon through analytical techniques such as SEM, XRF, AFM, and MP-AES, and to find new plating processes to reduce and limit the nickel release from 316L stainless steel.

## 2. Materials and methods

### 2.1. Samples preparation

Samples to be plated were cut out of an AISI 316L SS slab (thickness = 1 mm). A 2.00 mm diameter circular hole was mechanically made in the upper part of each 5.0 × 2.0 cm<sup>2</sup> sample.

Commercial degreasing and electroplating solutions were used, all provided by Valmet Plating Srl (Calenzano, Italy). The operating conditions are optimized by the manufacturer to obtain a compact deposit, rapid deposition times and the required thicknesses.

- ATMET200 is a proprietary degreasing solution (NaOH 40 g/L, alkaline silicates 27 g/L, K<sub>4</sub>P<sub>2</sub>O<sub>7</sub> 8 g/L, pH > 13). Operative conditions: current density 4 A/dm<sup>2</sup>, working temperature 30 °C, working time 60 s (to electrochemically clean the sample surface).
- Nickel Wood plating bath: used for electroplating stainless steel (NiCl<sub>2</sub>·6H<sub>2</sub>O 220 g/L, HCl 100 mL/L, pH < 1); operative conditions: current density 2 A/dm<sup>2</sup>, working temperature 25 °C, deposition time 60 s.
- AURINOX, a proprietary nickel-free solution for direct electroplating gold onto stainless steel (KAu(CN)<sub>4</sub> 1.8 g/L, H<sub>2</sub>SO<sub>4</sub> 50 g/L, pH < 1). Operative conditions: current density 1 A/dm<sup>2</sup>, working temperature 25 °C, deposition time 60 s.
- CUSTAR is a proprietary acid copper electroplating solution (CuSO<sub>4</sub>·5H<sub>2</sub>O 200 g/L, H<sub>2</sub>SO<sub>4</sub> 65 g/L, HCl 0.1 g/L, pH < 1). Operative conditions: current density 4 A/dm<sup>2</sup>, working temperature 22 °C, deposition time 30 min.
- BROMETN05 is a proprietary white bronze electroplating solution (CuCN 13 g/L, K<sub>2</sub>Sn(OH)<sub>6</sub> 40 g/L, Zn(CN)<sub>2</sub> 4 g/L, KCN 70 g/L, KOH 11 g/L, pH 13). Operative conditions: current density 1 A/dm<sup>2</sup>, working temperature 60 °C, deposition time 120 s.
- PALMET860 is a proprietary palladium-iron electroplating solution (Pd(NH<sub>3</sub>)<sub>4</sub>SO<sub>4</sub> 4 g/L, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> 2.5 g/L, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> 100 g/L, pH 7.5). Operative conditions: current density 1 A/dm<sup>2</sup>, working temperature 50 °C, deposition time 90 s.
- K2N is a proprietary gold electroplating solution (KAu(CN)<sub>2</sub> 3.7 g/L, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> 1.8 g/L, K<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> 100 g/L, C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> 80 g/L, pH 4). Operative conditions: current density 1.5 A/dm<sup>2</sup>, working temperature 40 °C, deposition time 90 s.

The EX354RD DUAL power supply (280 W) was used for all the experiments in galvanostatic mode (i.e., cathodic alkaline electrochemical degreasing, nickel, gold, white bronze, and Pd-Fe electroplating). Electroplating was performed within 500 mL beakers using a two-electrode setup. The counter electrode (anode) was a bare nickel plate in the case of nickel plating, a phosphorous-copper alloy slab in the case of copper plating, and a mixed metal oxide (MMO) mesh for the other depositions.

To investigate the nickel release mechanism, samples with physical vapor deposition (PVD) were also prepared with the following procedure: the 316L SS samples were initially degreased with ATMET200 solution, afterward they were cleaned in an ultrasonic bath for 10 min with acetone (ACS purity grade) and then ultrapure water. The surface was blown dry with nitrogen gas, and all samples were left for 30 min in an oven at 100 °C. PVDs were performed out in a Fission-Magnetron Sputtering System, HEX series (Korvus Technology. Ltd., Newtonington, UK) equipped with a direct current (DC) magnetron sputtering source. On the substrate, a thin adhesion

layer of chromium and a thick layer of gold were deposited. The circular targets of chromium and gold (50 mm diameter, 3 mm thick, 99.995 % purity, from Nanovision S.R.L) were sputtered in an argon atmosphere. Before deposition, the target was etched for 5 min with argon (Ar) to remove contaminants from the surface, during which the substrates were protected by a shutter placed between the substrate and the target. Ar was injected into the chamber with a flow rate of 30 Standard Cubic Centimeters per Minute (SCCM). The pressure was set at 0.65 Pa, and steel substrates were anchored to the rotating holder, with a speed of 15 RPM. In this position, the metals were intentionally deposited only on one side of the substrates. No external bias or temperature was applied to the sample. DC power was up to 5.0 W/cm<sup>2</sup> for chromium and 1.7 W/cm<sup>2</sup> for gold. The deposition time was 25 s for Cr and 11 min for Au.

After the preparation, all the samples were visually inspected to confirm the quality of the coating. One sample for each sample set was examined also with SEM and was tested to ensure the adhesion of the film before the Ni release test. In all cases the surface of the samples appeared without crack and free of defects. The adhesion of the layers was ensured with the cross-cut adhesion tape test (ISO 2819: 2018 and ISO 2409:2019), in any case we observed the detachment of the coating.

## 2.2. Sample characterization

A Hitachi SU3800 scanning electron microscope (SEM) was used to investigate the surface morphology both before and after the nickel release test.

The thickness of the deposited films was measured with a Bowman B Series X-ray Fluorescence (XRF) spectrometer using an acquisition time of 60 s, 50 kV tube voltage, 0.8 mA tube current, and a collimator of 0.6 mm in diameter.

Molecular Imaging PicoSPM atomic force microscopy (AFM), with a triangular Si<sub>3</sub>N<sub>4</sub> cantilever (Veeco, NP-S10, Munich, Germany), was employed to evaluate the surface roughness of the samples in terms of average roughness (Sa) and root mean square roughness (Sq).

## 2.3. Nickel release

The samples were tested for nickel release according to EN 1811:2023. To obtain a statistical figure, three samples were evaluated for each series, and the results are reported as an average value and standard deviation. The release solutions were analyzed by MP-AES to measure the nickel released, defined as µg/cm<sup>2</sup>/week. The samples were initially cleaned with a 0.5 % solution of sodium dodecyl sulfate (SDS). According to this regulation, the tested articles were suspended in a suitable container, dipped in an artificial sweat solution consisting of 0.5 % NaCl (Carlo Erba), 0.1 % urea (Sigma-Aldrich), and 0.1 % lactic acid (Thermo Scientific) dissolved in water [20]. The pH was adjusted to 6.5 ± 0.1 with 0.1 M NaOH (Carlo Erba) or 0.1 M HCl (VWR Chemical Prolabo) solutions. The volume of the test solution added corresponds to 1 mL/cm<sup>2</sup> of the test area. The articles were kept in this solution for one week; after this period, they were removed and rinsed with water. The release solutions were analyzed to measure the nickel released, defined as µg/cm<sup>2</sup>/week.

The EN 1811:2023 standard was used as a reference test method. For comparison, the EN 16128:2015 procedure was also performed on the samples. This is the specific reference method for nickel release from spectacle frames. The two procedures are similar; the same artificial sweat formulation is used, but instead of suspending the sample in the solution, a blotting paper soaked with the solution is used. The blotting paper consists of pure cellulose with one side covered with polyethylene. As suggested in the standard, LabSorb Ultra test paper (Sartorius-Stedim Biotech) was used. The paper was previously cut to a size that could totally cover the sample and then fully soaked in the artificial sweat solution. Each sample in contact with the paper was sealed inside with Parafilm and then placed in an oven (Memmert climate chamber) for seven days at 30 °C and 95 % RH. At the end of the seven days, the paper was removed from the samples and placed inside test tubes containing 10 mL of a 2 % HNO<sub>3</sub> (Carlo Erba) solution. These tubes were subjected to 15 min of sonication (VEVOR Digital Ultrasonic Cleaner) to extract the nickel contained within the paper. Any instrument used during these steps did not have to contaminate the analysis. The limit value for nickel release defined by this standard is 0.5 µg/cm<sup>2</sup>/week.

An Agilent 4200 Microwave Plasma Atomic Emission Spectrometer (MP-AES) based on nitrogen plasma (Santa Clara, CA, USA) was used to measure the amount of nickel released in test solutions (CCD detector with a detection limit of 25 ppb). In the manuscript the only average values are reported, all the data recorded have been listed in the supplementary materials.

The workflow of this study can be schematized as follows:

1. 316L SS samples were characterized after the degreasing procedures and specific deposition processes with SEM, XRF, and AFM.
2. Each sample was tested for nickel release, according to the regulation EN 1811:2023.
3. After one week in the test solution, samples were rinsed with water and analyzed by SEM to identify surface changes due to the test performed.
4. The release solution was analyzed by MP-AES to measure the nickel released.

## 3. Results and discussion

### 3.1. Pre-galvanization treatments

It is well known that 316L stainless steel, in its original state, does not release nickel (Ni<sup>2+</sup> < 0.025 µg/cm<sup>2</sup>/week in sodium chloride 0.05 M and in synthetic sweat solutions [18]). We also tested the nickel release of 316L samples as they are and verified that no nickel

was released. The nickel release does not occur due to the chromium oxide layer that naturally passivates the surface.

The role of the electrochemical degreasing process in nickel release from 316L SS was evaluated. This process, necessary for proper electroplating, is usually performed for 60 s at 4 A/dm<sup>2</sup>. To evaluate whether the electro-degreasing process could influence nickel release, we performed this step by varying the current density during degreasing with ATMET200 solution: three different current densities were investigated—1 A/dm<sup>2</sup>, 20 A/dm<sup>2</sup>, and 100 A/dm<sup>2</sup>.

After the degreasing step, samples were rinsed in a “neutralization” solution made of H<sub>2</sub>SO<sub>4</sub> 5 %. To evaluate the impact of this step as well, two sets of samples were studied for each chosen current density: one set dipping the samples into the neutralization solution, and one set skipping this step before dipping the samples in the nickel release test. All samples were tested for nickel release according to the regulation EN 1811:2023.

Regardless of the current density used, with or without neutralization, no apparent changes were observed on the surface of the samples after performing the nickel release test. The electrochemical degreasing does not lead to an increase in nickel release; indeed, the values of nickel obtained are below the detection limit of MP-AES, corresponding to a release lower than 0.025 µg/cm<sup>2</sup>/week, far less than the 0.2 µg/cm<sup>2</sup>/week limit. This is probably because the electrochemical degreasing process is not able to remove the chromium oxide layer that passively covers the SS surface, so the substrate remains fixed, and nickel release does not occur.

### 3.2. Electroplated stainless steel samples

Once verified that stainless steel 316L does not release nickel, both as it is and after electrochemical degreasing, we studied electroplated SS samples. The most widespread solution for electroplating SS is the nickel Wood’s bath, which can deposit a thin layer (“strike”) of nickel on SS [8]. In this study, we compared that solution to the innovative and Ni-free electroplating formulation for 316L SS, called AURINOX. AURINOX enables the direct electroplating of a gold strike onto the surface of stainless steel, making it prone to electroplating without the use of nickel. The performances of these two electroplating solutions were compared in terms of nickel release, investigating how surface roughness and electroplating processes participate in nickel release from 316L SS.

#### 3.2.1. Unpolished stainless steel

Surface roughness of unpolished 316L stainless steel was investigated by using AFM (Fig. 1). AFM roughness analysis showed that unpolished 316L SS had high roughness values: Sq = 15.3 nm and Sa = 9.7 nm.

Unpolished 316L SS samples were electrochemically degreased, dipped in a neutralization solution, and then activated for electroplating using either nickel strike (Wood’s bath) or gold strike (AURINOX) as adhesion layers. A thicker layer of gold was then deposited using the K2N bath, producing two sets of samples: “Ni Wood/Au” and “AURINOX/Au”.

Layer thickness was measured by means of the XRF technique: Ni 0.03 ± 0.01 µm, Au 0.29 ± 0.01 µm for set “Ni Wood/Au,” and Au 0.31 ± 0.02 µm for set “AURINOX/Au”.

All samples were assessed for nickel release according to the regulation EN 1811:2023. The results are expressed as average values and standard deviation of three repetitions. The nickel released from samples “Ni Wood/Au” was 1.86 ± 0.23 µg/cm<sup>2</sup>/week, while for samples “AURINOX/Au” it was 0.99 ± 0.19 µg/cm<sup>2</sup>/week.

Replacing the nickel strike adhesion layer with the gold strike allowed the quantity of nickel released to halve, reducing from 1.86 µg/cm<sup>2</sup>/week to 0.9 µg/cm<sup>2</sup>/week. However, in both cases, the amount of nickel released is above the limit imposed by the regulation. Although the release of nickel from the “Ni Wood/Au” samples is not desirable, this could be explained by considering that the release occurs from the Ni layer. On the other hand, the release from the “AURINOX/Au” samples is counterintuitive. In these samples, nickel is only present in the substrate; therefore, it is evident that the release occurs from the SS. This result is unexpected if we consider that bare steel does not release nickel: hence further studies are required.

Therefore, we suspected that surface activation might play a pivotal role concerning nickel release. Indeed, by removing the outermost chromium oxide layer before plating, it turns out that the underlying chromium is no longer in contact with the air, and therefore, the passivation layer cannot be reformed. The synthetic sweat solution could attack the substrate by passing through microchannels within the porous gold layer [21,22]. The presence of tensions inside the galvanic layer could be increased by imperfect adhesion to the substrate, which tends to be passivated during the activation process. The electrical contact of SS with a nobler metal

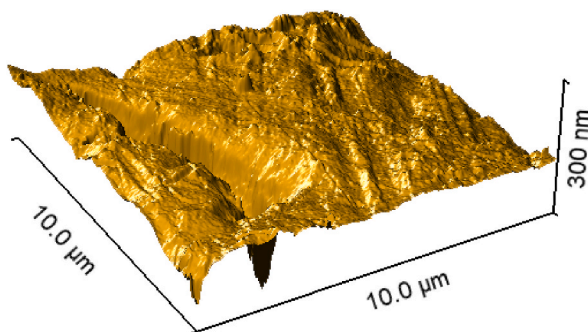


Fig. 1. Unpolished 316L stainless steel surface, acquired by AFM.

like gold could even increase the corrosion process due to galvanic corrosion. Furthermore, the high surface roughness of the unpolished SS substrate may hinder a homogeneous coverage of the substrate. Nickel could also migrate from the substrate to the surface through the gold layer by an intermetallic diffusion mechanism [23].

The greater release of nickel from the “Ni Wood/Au” samples can be explained by considering a greater presence of this metal due to the electrodeposited Ni layer.

SEM analysis performed on the samples after the nickel release test (Fig. 2) showed the detachment of the coating in many spots.

In “Ni Wood/Au” samples, cracks in the deposit are clearly visible, and nickel has likely been released from these cracks, indicating an adhesion and tensile stress-related problem.

### 3.2.2. Polished stainless steel

The roughness was demonstrated to have an effect on pitting corrosion of SS [24]. Based on the nickel release results obtained for unpolished and electroplated SS samples, we repeated the measurements on polished samples to verify if there were any dependencies on the release results from the sample’s surface roughness. The samples were polished using a conventional polishing machine with a rotating cotton disk and polishing compound. The surface roughness of polished 316L SS was evaluated with AFM analysis (Fig. 3). As expected, we measured lower values of roughness for polished sample than for unpolished samples:  $S_q = 4.1$  nm and  $S_a = 3.2$  nm.

Polished 316L SS was electrochemically degreased and then electroplated. For comparison with unpolished samples, the same two sets of samples were prepared following the procedure described in the previous section, depositing a nickel strike or gold strike followed by a thick gold layer. Samples are named “P-Ni Wood/Au” and “P-AURINOX/Au”, where the prefix “P” indicates that the sample’s surface has been previously polished.

The thickness of the layers was measured with XRF: Ni  $0.06 \pm 0.01$   $\mu\text{m}$ , Au  $0.24 \pm 0.03$   $\mu\text{m}$  for set “P-Ni Wood/Au”, and Au  $0.25 \pm 0.02$   $\mu\text{m}$  for set “P-AURINOX/Au”.

All samples were assessed for nickel release according to the regulation EN 1811:2023. The data obtained are expressed as an average value and standard deviation of three samples. The nickel released from samples “P-Ni Wood/Au” was  $1.43 \pm 0.76$   $\mu\text{g}/\text{cm}^2/\text{week}$ , while for samples “P-AURINOX/Au” it was  $0.10 \pm 0.07$   $\mu\text{g}/\text{cm}^2/\text{week}$ . It is evident that the samples with the nickel strike layer failed the test, even if with a lower release if compared to the unpolished samples, while the sample with the gold adhesion layer passed the test, confirming that the surface roughness of the samples has an important effect.

The SEM analysis performed after the nickel release test on the polished samples (Fig. 4) revealed a clear difference compared to the unpolished samples, with a significantly lower presence of defects. The “P-Ni Wood/Au” sample exhibits a higher presence of corrosion products compared to the “P-AURINOX/Au” sample.

The gold strike adhesion layer ensured better endurance compared to the nickel Wood’s bath, since the released  $\text{Ni}^{2+}$  value dropped from  $1.43$   $\mu\text{g}/\text{cm}^2/\text{week}$  for the traditional Ni-based bath to  $0.10$   $\mu\text{g}/\text{cm}^2/\text{week}$  for our Ni-free process.

### 3.2.3. Full electroplating cycles

Productive cycles effectively used at an industrial level typically involve the deposition of multiple layers of different metals to guarantee better performance in terms of wear durability, corrosion resistance, brightness, and color to the final product. For this reason, we decided to replicate the nickel release analysis also on samples subjected to a full electroplating cycle: copper (Cu); bronze; palladium (Pd); gold (Au). The polished 316L stainless steel samples were electroplated with a traditional Ni-based cycle (P-Ni Wood/Cu/Bronze/Pd/Au) and with the Ni-free cycle (P-AURINOX/Cu/Bronze/Pd/Au), using galvanic solutions Ni Wood, AURINOX, CUSTAR, BROMETN05, PALMET860, and K2N. The prefix “P” indicates the polished surface of the samples.

Thickness determination by XRF gave Cu  $20.0 \pm 0.5$   $\mu\text{m}$ , bronze  $0.80 \pm 0.01$   $\mu\text{m}$ , Pd  $0.26 \pm 0.01$   $\mu\text{m}$ , and Au  $0.25 \pm 0.01$   $\mu\text{m}$  for both sets of samples.

All samples were tested for nickel release, according to the regulation EN 1811:2023. The data obtained are expressed as the average value and standard deviation of three samples. The nickel released from samples “P-Ni Wood/Cu/Bronze/Pd/Au” was  $6.02 \pm$

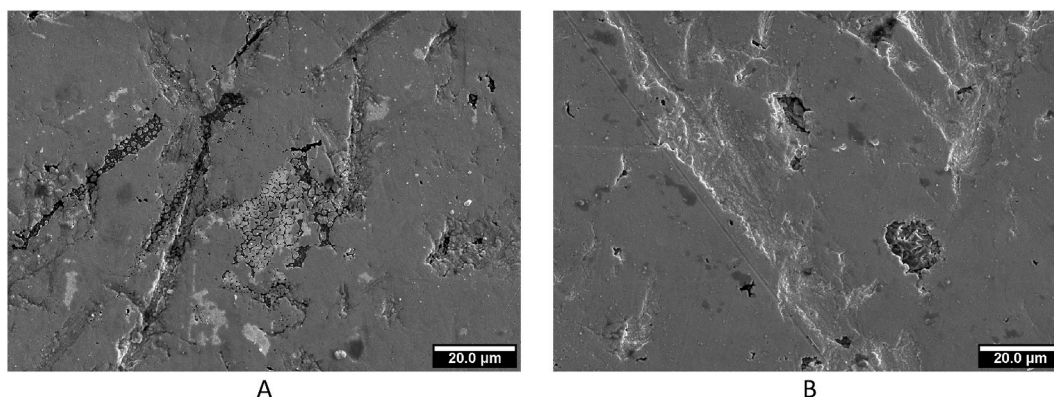


Fig. 2. SEM analysis of sample A) Ni Wood/Au and B) AURINOX/Au after the nickel release test.



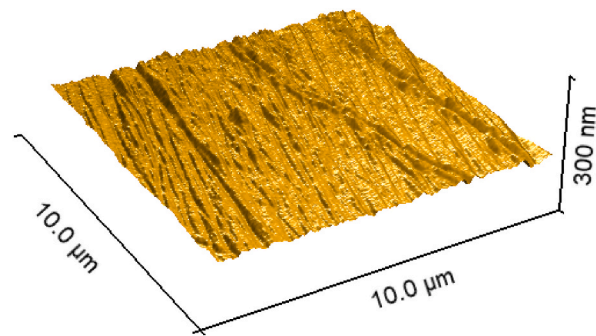


Fig. 3. Polished 316L stainless steel surface, acquired by AFM.

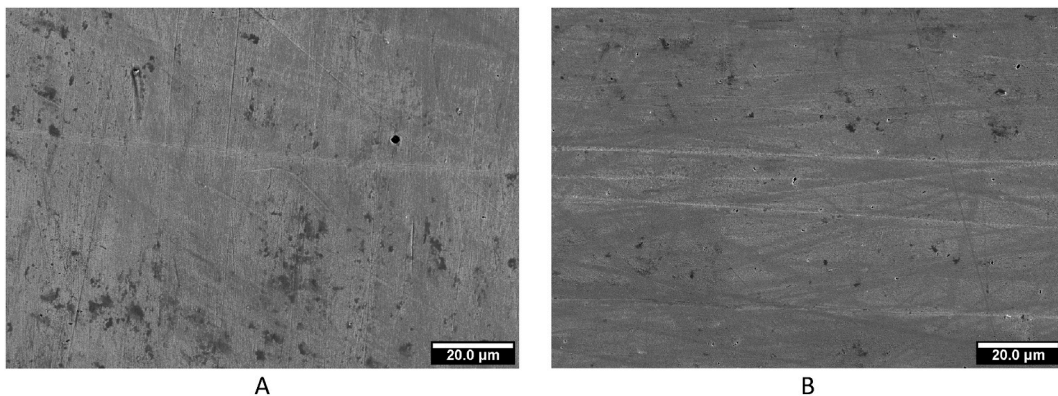


Fig. 4. SEM analysis of sample A) P-Ni Wood/Au and B) P-AURINOX/Au after the nickel release test.

$0.08 \mu\text{g}/\text{cm}^2/\text{week}$ , while for samples “P-AURINOX/Cu/Bronze/Pd/Au” was  $1.22 \pm 1.25 \mu\text{g}/\text{cm}^2/\text{week}$ .

From these results we can draw these considerations: both processes failed the test, unexpectedly releasing even more nickel than the first “Ni Wood/Au” samples, suggesting that increasing the number of layers does not limit the release process but instead may even worsen it by introducing additional adhesion and tensile stress variables. Anyway, it is evident that the presence of the gold strike layer had a much lower release of nickel than the use of a nickel strike, indicating the promising features of AURINOX. Furthermore, by looking at the standard deviation of the results, the samples with the nickel adhesion layer release almost all the same amount whereas the samples with the gold strike are much more variable. In one out of the three repetitions of the Ni-free cycle samples, the released nickel was even below the instrument detection limit, leaving room for further improvement.

Since in the full plating cycle, the distance from the steel surface to the external environment is several microns, the hypothesis that the release of nickel is due to intermetallic diffusion through the deposited layers can be discarded. In fact, diffusion times are significantly longer at room temperature than the time elapsed between the sample preparation and the end of the release test [25].

SEM analysis performed after the nickel release test (Fig. 5) showed many cracks in the coating and severe detachment of the

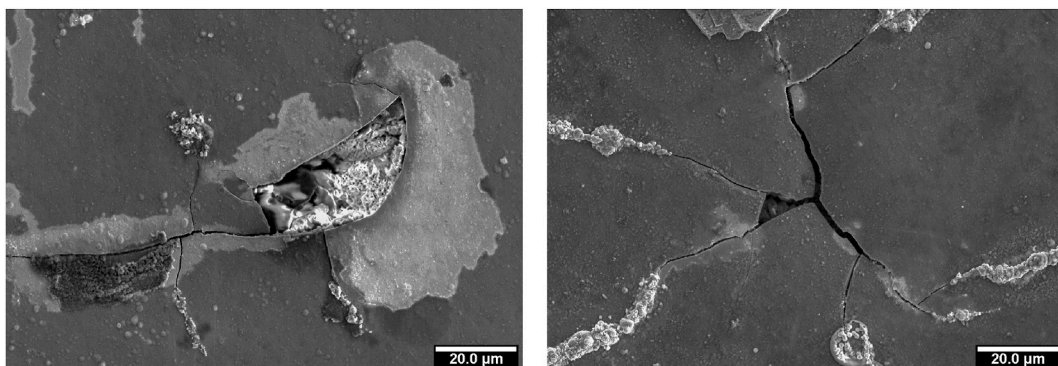


Fig. 5. SEM analysis of sample A) P-Ni Wood/Cu/Bronze/Pd/Au and B) P-AURINOX/Cu/Bronze/Pd/Au after the nickel release test.

deposited layers; moreover, it is evident the presence of corrosion products mainly caused by electrodeposited copper that comes out from below the surface, spreading on the sample surface.

Since electroplating stainless steel requires removing the chromium oxide layer that passivates the surface, nickel release seems inevitable. The presence of a full galvanic cycle increases nickel release from 316L stainless steel.

We tried to overcome this issue by increasing the thickness of the top layer of precious metal. New, polished 316L stainless steel samples were electroplated with the same two cycles described above. Unlike the previous samples, in this case, a thicker layer of gold was deposited on top of the samples. Gold deposition was performed using the same solution and conditions described in the experimental section except for the time deposition, which was 6 min, for depositing 1  $\mu\text{m}$  of gold. These sets of samples were named “P-Ni Wood/Cu/Bronze/Pd/Au(1)” and “P-AURINOX/Cu/Bronze/Pd/Au(1)”.

Again, XRF confirmed the thickness of the electroplated layers for both sets of samples: Cu  $20.0 \pm 0.5 \mu\text{m}$ , bronze  $0.80 \pm 0.01 \mu\text{m}$ , Pd  $0.26 \pm 0.01 \mu\text{m}$ , and Au  $1.00 \pm 0.01 \mu\text{m}$ .

All samples were tested for nickel release, according to the regulation EN 1811:2023. The data obtained are expressed as an average value and standard deviation of three samples. The amount of nickel released from samples “P-Ni Wood/Cu/Bronze/Pd/Au(1)” was  $0.19 \pm 0.18 \mu\text{g}/\text{cm}^2/\text{week}$ , while for samples “AURINOX/Cu/Bronze/Pd/Au(1)” was  $0.14 \pm 0.03 \mu\text{g}/\text{cm}^2/\text{week}$ . In both cases, the nickel release of electroplated 316L SS was below the threshold value allowed by current legislation, and no surface changes were observed at SEM after the nickel release test was performed. It has been proven that a thicker top layer of gold can avoid nickel release from 316L SS, even if it is electroplated using a Ni-based cycle. These results seem to confirm the hypothesis that the release is due to the porosity of the coating: in fact, it is known that thicknesses of gold lower than 0.8  $\mu\text{m}$  are typically porous [22]. SEM analysis of these samples performed after the nickel release test (Fig. 6) showed a surface unaltered.

### 3.3. Comparison of different release tests

The EN 1811:2023 standard was used as a reference test method; for comparison, the EN 16128:2015 procedure was also performed on some samples. This is the specific reference method for the nickel release from spectacle frames. The two procedures are similar: both use the same artificial sweat as a test solution with the same incubation time (one week). The only difference is that in EN 1811, the samples are suspended in the solution, while in EN 16128, samples are covered with blotting paper soaked with the solution, then the released nickel is extracted with an acid solution. We performed this test to evaluate if the different procedures could have an impact on the release evaluation.

We evaluated uncoated 316L steel, “P-Ni Wood/Cu/Bronze/Pd/Au”, and “P-AURINOX/Cu/Bronze/Pd/Au” samples. According to EN 16128:2015, the limit value for nickel release, as defined by the European regulation, is  $0.5 \mu\text{g}/\text{cm}^2/\text{week}$ . We obtained a nickel release of  $0.03 \pm 0.04 \mu\text{g}/\text{cm}^2/\text{week}$  for base 316L SS;  $0.06 \pm 0.08 \mu\text{g}/\text{cm}^2/\text{week}$  for “P-Ni Wood/Cu/Bronze/Pd/Au”;  $0.28 \pm 0.31 \mu\text{g}/\text{cm}^2/\text{week}$  for “P-AURINOX/Cu/Bronze/Pd/Au”. All the samples pass the test with release values tens of times lower compared to EN 1811 performed on the same set of samples. The results show that EN 16128 subjects the samples to milder conditions compared to EN 1811.

### 3.4. Mechanism of Ni release from plated steel

The release data previously obtained on different finishes led us to suppose that plated SS may, in some cases, release nickel, contrary to non-galvanized steel, due to the necessary activation of the substrate with the removal of the chromium oxide layer, combined with the porosity of the electrodeposited layers. To confirm this hypothesis, new samples were made following a completely different process. Through PVD, it is possible to conduct the deposition directly on a substrate, even a non-conductive one. Therefore, the gold was deposited onto steel (after the deposition of a thin chromium adhesion layer) without removing the passivating layer of chromium oxide. This set of samples is named “PVD-Au”. The PVD deposition was performed only on one side of the samples, leaving a

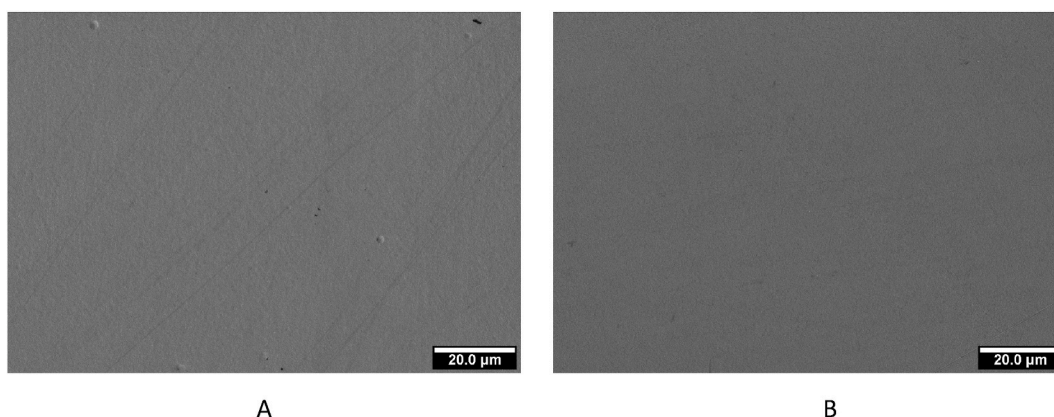


Fig. 6. SEM analysis of sample A) P-Ni Wood/Cu/Bronze/Pd/Au(1) and B) P-AURINOX/Cu/Bronze/Pd/Au(1) after the nickel release test.

wide SS surface exposed for the EN 1811 releasing test.

The thickness of the Au layer measured with XRF was  $0.49 \pm 0.01 \mu\text{m}$ .

The nickel release of all the “PVD-Au” samples was below the detection limit of MP-AES, corresponding to a release lower than  $0.025 \mu\text{g}/\text{cm}^2/\text{week}$ , far less than the  $0.2 \mu\text{g}/\text{cm}^2/\text{week}$  limit. All the nickel release results obtained in this study are summarized in Fig. 7.

Based on the obtained results, we can state that the activation process for electroplating of SS, which involves the removal of the chromium oxide layer, is central to the release of nickel. 316L SS itself does not release nickel due to the passivation layer that covers it. Cathodic electrolytic processes, such as degreasing, may affect this layer, but as soon as the current is disconnected, the steel in contact with oxygen quickly passivates again. The deposition of a metallic layer like gold prevents the steel from passivating. Since it is known that electrodeposition produces porous layers, the presence of a small defect can initiate a localized corrosion process (Fig. 8A), favored by a high ratio between the cathodic surface (Au) and the anodic surface (SS) [22].

It has been verified that higher thicknesses of the noble metal prevent the release of nickel since the presence of open channels between the substrate and the electrolyte through the coating is less likely (Fig. 8B). The development of electrodeposition processes that allow for reduced deposit porosity through new formulations [26] or pulsed currents may lead to similar beneficial results with the use of less material [27].

The use of a rougher substrate has shown a higher release of nickel. This can be explained by considering the issue of the point effect to which galvanic depositions are subject: at the micrometric level, higher thicknesses are obtained in areas of high current density compared to areas of low current density. In a rough substrate, this effect will be greater than in a less rough substrate. Thus, even with the same average deposited thickness, a rougher substrate will have areas where the thickness is significantly lower, favoring localized corrosion phenomena.

Finally, by depositing gold via PVD directly onto steel without removing the passivation layer, we verified that it is precisely this layer that prevents the release of nickel. PVD deposits have columnar growth, and the presence of open porosity is more likely to occur [28,29]. Additionally, part of the steel surface was intentionally not covered. Despite this, the samples did not release nickel thanks to the remaining chromium oxide layer (Fig. 8C).

#### 4. Conclusions

Stainless steel is a highly valuable material due to its properties and sustainability, making it suitable for many applications, including direct contact and penetration skin. Although stainless steel is generally considered safe regarding nickel release, our study demonstrates that electroplating, even with nickel-free processes, can induce significant nickel release. In this study we found that smoother substrates and increased noble metal thicknesses effectively prevent the release of nickel. The metal release was found to be primarily caused by the removal of the naturally occurring passivation layer of stainless steel and the microporosity of electroplated coatings. This study reveals an overlooked issue: stainless steel, under certain conditions, can pose risks related to nickel release. Our findings not only improved the understanding of this phenomenon, but also suggested practical solutions that deserve to be further explored in future research.

#### Funding

Project funded under the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3 - Call for tender No. 341 of March 15, 2022 of Italian Ministry of University and Research (MUR) funded by the European Union - NextGenerationEU - Project code PE\_00000004, CUP B83C22004890007, Project title “3A-ITALY - Made-in-Italy circolare e sostenibile”. The authors also thanks for the support offered by fondazione CR Firenze, fondazione per la ricerca e l'innovazione and confindustria Firenze within the FABER3 project and for financial support of the PhD fellowship PON Research and Innovation 2014–2020 (D.M 1061/2021) XXXVII Cycle in Chemical Sciences.

#### Data availability statement

Data included in article/supp. material/referenced in article.

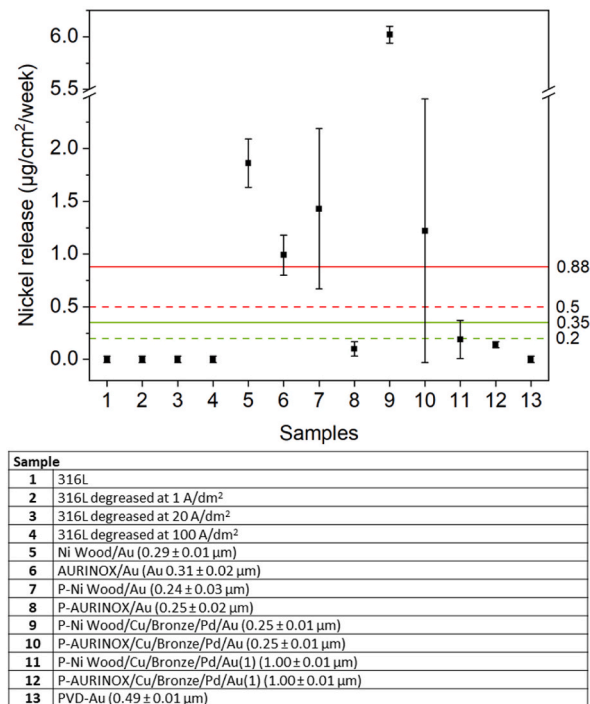
#### CRediT authorship contribution statement

**Roberta Emanuele:** Writing – original draft, Investigation. **Andrea Comparini:** Investigation. **Margherita Verrucchi:** Writing – review & editing. **Ivan Del Pace:** Supervision. **Arianna Meoli:** Investigation. **Mariya Vorobyova:** Investigation. **Walter Giurlani:** Writing – review & editing, Writing – original draft, Validation, Supervision, Conceptualization. **Massimo Innocenti:** Supervision, Project administration, Funding acquisition.

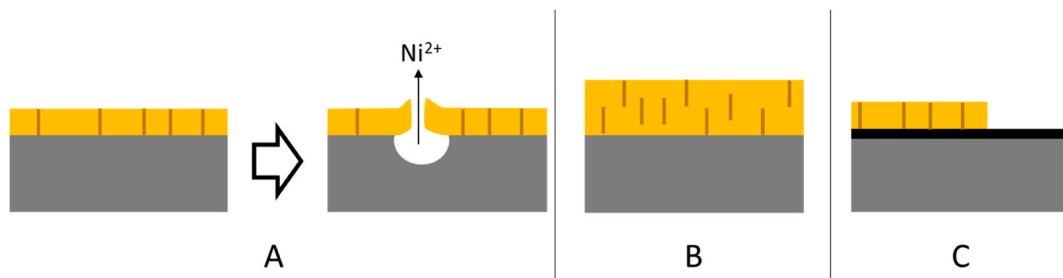
#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.





**Fig. 7.** Nickel release from each sample discussed in this study, expressed as average and standard deviation of three repetitions. The thickness of the final gold layer is reported in the brackets).



**Fig. 8.** Schematic cross-sectional illustration of A) a thin electrodeposited gold layer on SS in which the presence of open porosity leads to localized corrosion and nickel release; B) a thick electrodeposited gold layer that prevents nickel release; C) a thin and partial covering PVD gold layer on passivated SS that prevents the nickel release.

### Acknowledgments

The authors acknowledge the support that has been given from Valmet Plating Srl from a technical point of view as well as in providing materials and chemicals.

### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2024.e37125>.

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