Electroplated Tin-Nickel Coatings as a Replacement for Nickel to Eliminate Nickel Dermatitis

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Introduction:

Professor Corrosion & Surface Technology
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Initiator and manager of several research projects: electro-catalytic materials for hydrogen production, catalytic material for methanization, antibacterial surfaces electro-catalytic and photo-catalytic, low friction coating for combustion engines, nickel dermatitis/replacement, corrosion of medical implants in vivo and in vitro etc.

130 scientific articles and 25 patents

Book: Advanced surface Technology "A holisic view on the extensive and intertwined world of applied surface engineering" by Per Møller & Lars Pleth Nielsen
Nickel dermatitis (skin allergy) is a growing problem in numerous countries. The alarming frequency of sensitization to nickel especially in the US caused nickel to be selected as the “Allergen of the Year” in 2008 by the American Contact Dermatitis Society. Nickel as coating in contact with skin has already been regulated by the nickel EU directive [94/27/EC] since 1994. In the present contribution tin/nickel alloy coatings (66.9 wt. % Sn), electrodeposited from a chloride/fluoride containing alloy electrolyte, will be presented as an alternative for both nickel and bright chromium coatings.
Nickel dermatitis
Nickel dermatitis
Press focuses on nickel dermatitis

Nickel allergy

Nickel allergy is one of the most common causes of allergic contact dermatitis — an itchy rash that appears when your skin touches a usually harmless substance. Nickel allergy is commonly associated with earrings and other jewelry for body piercings. But nickel can be found in many everyday items — from coins to necklace clasps, from watchbands to eyeglass frames.

Nickel allergy can affect people of all ages. A nickel allergy usually develops after repeated or prolonged exposure to nickel in everyday items. Nickel allergy can cause itching, swelling, and redness. Nickel allergies may cause skin rashes, blisters, and other symptoms. If you have a nickel allergy, you should try to avoid contact with nickel.
Nickel allergy is one of the most common causes of allergic contact dermatitis — an itchy rash that appears when your skin touches a usually harmless substance. Nickel allergy can affect people of all ages. A nickel allergy usually develops after repeated or prolonged exposure to items containing nickel. Treatments can reduce the symptoms of nickel allergy. Once you develop nickel allergy, however, you will always be sensitive to the metal and should avoid contact.

Cited CNN
Nickel may be released from laptop computers

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Key words: consumer; dermatitis; nickel.

Each solution in succession on a white cotton wool-tipped applicator, which was rubbed for up to 20 seconds against the test object. A positive reaction was indicated by the coloration of the applicator, and a negative reaction was registered when no color change was observed. Doubtful reactions, defined as a pink color or discolouration possibly masking a pink colour, were performed, and if the reaction remained unaltered to be doubtful. We tested
The history and the interest of Tin/Nickel

The Tin/Nickel Alloy & The Tin/Nickel Process

Tin/Nickel and Nickel – allergic (contact dermatitis)?

Corrosion properties of Tin/Nickel
Tin/Nickel was first time described of Monk and Ellingham 1935

Later a process was developed by Tin Research Institute and published

Tin/Nickel coated braas immersed in Nitric acid

HNO$_3$
Tin/Nickel

Sn/Ni plated brass

Stainless steel pipe for draught beer
The history and the interest of Tin/Nickel

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Tin/Nickel and Nickel – allergic (contact dermatitis)?

Corrosion properties of Tin/Nickel
65% w/w tin and 35% w/w nickel.
The crystal structure of the Electrodeposited Sn/Ni was early stated to have a hexagonal structure like Cu₆Sn₅ of the type NiAs (B8₁) Structure
The process is based on an acid chloride/fluoride electrolyte which give the single phase intermetallic compound NiSn containing approximately 65% w/w tin and 35% w/w nickel.

**Composition**

- Ni: 60-65 g/l
- Sn: 20-25 g/l
- Stabilizer: 30 g/l
- pH: 4 - 4.6
X-ray diffraction patterns (CuK$_\alpha$) of electrodeposited NiSn on nickel substrate
X-ray diffraction patterns (CuK\textsubscript{\(a\)}) of electrodeposited NiSn on nickel substrate

Conclusion: A hexagonal structure like described earlier

Results from The Technical University of Denmark
CONTENT

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Corrosion properties of Tin/Nickel
Danish law: (BEK nr 854 af 16/12/1991)

Departmental order about embargo for sales of “special products” of nickel or nickel alloys, which could release more than 0.5 μg Ni/cm²/week
Nickel dermatitis from contact with jeans studs (left) and necklace (right)


Nickel dermatitis from contact with nickel plated paint spray gun.
The presence of a rash under an individual allergen indicates sensitivity to this substance. This does not prove that this particular allergen is the cause, but may provide a clue of what may be causing the problem.

Patch tests on the back
Patch tests on the back

Nickel coated brass
Patch tests on the back

Stainless steel 316
Patch tests on the back
Patch tests on the back

Patch test results.
The body's immune system recognizes allergen as "foreign". When this happens, white cells are attracted from the blood into the skin over several days. This results in inflammation and the development of a rash.
Artificial sweat 0,5% NaCl, 0,1% milk-acid and 0,1% urea. pH correction with ammonia to 6,5.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Nickel content in %</th>
<th>Release in microgram pr cm² pr week in the beginning</th>
<th>Release in microgram pr cm² pr week after 3 weeks.</th>
<th>Allergic skin reaction from persons with nickel allergy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elektrolytic nickel</td>
<td>100</td>
<td>10</td>
<td>70</td>
<td>75</td>
</tr>
<tr>
<td>Nickel/Tin</td>
<td>35</td>
<td>0,5</td>
<td>0,1</td>
<td>22</td>
</tr>
<tr>
<td>Coin metal</td>
<td>25</td>
<td>6</td>
<td>3 (not measured)</td>
<td></td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>9</td>
<td>0,04</td>
<td>0,01</td>
<td>3</td>
</tr>
<tr>
<td>White Gold</td>
<td>15</td>
<td>0,3</td>
<td>0,02</td>
<td>11</td>
</tr>
<tr>
<td>Tin coating on copper</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>10</td>
</tr>
</tbody>
</table>

The history and the interest of Tin/Nickel

The Tin/Nickel Alloy & The Tin/Nickel Process

Tin/Nickel and Nickel – allergic (contact dermatitis)?

Corrosion properties of Tin/Nickel

Conclusion
Corrosion potential of Tin/Nickel alloy compared with selected metals.
Corrosion potential of Tin/Nickel alloy compared with selected metals.

50 mV is needed to generate a corrosion.
Corrosion potential of Tin/Nickel alloy compared with selected metals.
Galvanic current, gold

- Sn/Ni
- Au

Diagram showing the galvanic current over time with a linear scale for both current [mA/cm²] and time [s]. The graph indicates a decrease in current with increasing time. The line is labeled "NiSn, Au."
Galvanic current, silver

Current [mA/cm²]

Time [s]
Galvanic current, DLC

- NiSn, Ag
- NiSn, Au
- NiSn, DLC

Current [mA/cm^2] vs. Time [s]
Galvanic current, copper

Current [mA/cm²] vs Time [s]

- NiSn, Ag
- NiSn, Au
- NiSn, Cu
- NiSn, DLC

About 0.1 μA/cm²
Polarization curves for tin/nickel

Test solution 3% NaCl in an acetate buffer pH = 6
Polarization curves for tin/nickel & gold

Potential SHE [mV] vs. Current [mA/cm²]

NiSn  
Au  

Basematerial 904
Polarization curves for tin/nickel & gold

Potential SHE [mV] vs. Current [mA/cm²] for Basematerial 904.

Lines:
- **NiSn+Au** (Blue)
- **NiSn** (Green)
- **Au** (Red)

The graph shows the polarization behavior of tin/nickel and gold on Basematerial 904.
Multielement Pourbaix diagramme for gold and chloride

Au - Cl - H2O - System at 25.00 C

<table>
<thead>
<tr>
<th>ELEMENTS</th>
<th>Molality</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>1.000E-06</td>
<td>1.000E+00</td>
</tr>
<tr>
<td>Cl</td>
<td>5.000E-02</td>
<td>1.000E+00</td>
</tr>
</tbody>
</table>
Multielement Pourbaix diagramme for gold and chloride

Au - Cl - H2O - System at 25.00 C

-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0

Eh (Volts)

AuCl$_2^-$

Au(OH)$_3$

Au

ELEMENTS
Au
Cl

Molality
1.000E-06
5.000E-02

Potential SHE [mV]

Current [mA/cm²]
Multielement Pourbaix diagramme for gold and chloride

- **Au** + 3H₂O = Au(OH)₃ + 3H⁺ + 3e⁻
- **Au** + 2Cl⁻ = AuCl₂⁻ + e⁻
- CH₃-COO⁻ + 2H₂O = 2CO₂(g) + 7H⁺ + 8e⁻

### Elements and Molality

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<tr>
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<tr>
<td>Cl</td>
<td>5.000E-02</td>
</tr>
</tbody>
</table>
Polarization of the gold layer

\[
\begin{align*}
\text{Potential SHE [mV]} & \quad \text{Current [mA/cm}^2\text{]} \\
\text{Au} & \quad \text{Sn/Ni} \\
\text{Stainless steel} & \quad \text{+}
\end{align*}
\]
Polarization of the gold layer

Sn/Ni

Stainless steel

Potential SHE [mV] vs. Current [mA/cm²]
The gold layer is stripped over time from the tin/nickel coating during the anodic polarization of the work electrode. In the third last pictures (to the right) the potential is close to +1000 mV (SHE) and the gold coating starts to corrode, forming colloidal Au(OH)$_3$ which start to discolor the work electrode.
Saltspray tests
Corrosion potential of Tin/Nickel alloy compared with selected metals.
Salt spray, week 1

st.37 + 30µm Ni + 1µm Cr

st.37 + 20-25µm Cu + 7-10µm NiSn

st.37 + 25 µm Cu + 15µm NiSn +

Cr on Ni

NiSn on Cu

Cr on NiSn
Salt spray, week 2

- **Cr on Ni**
  - st.37 + 30µm Ni + 1µm Cr

- **NiSn on Cu**
  - st.37 + 20-25µm Cu + 7-10µm NiSn

- **Cr on NiSn**
  - st.37 + 25 5µm Cu + 15µm NiSn +
Salt spray, 19 days

After 4 months no corrosion

- st.37 + 30μm Ni + 1μm Cr
- st.37 + 20-25μm Cu + 7-10μm NiSn
- st.37 + 25μm Cu + 15μm NiSn +

Cr on Ni | NiSn on Cu | Cr on NiSn
Conclusion

• Sn/Ni coatings cannot introduce nickel dermatitis

• The structure of electrodeposited equiatomic NiSn alloy was indicated in an X-ray diffraction pattern to mainly consist of a hexagonal structure of the NiAs type.

• Electrochemical results show that NiSn has a passive behaviour that exceeds that of stainless steel (904) in chloride electrolytes.

• Sn/Ni only give slow corrosion or none by galvanic coupling even with gold.

• Sn/Ni can be coated with Cr with good covering power using a new patented process and in this way replacing conventional bright chromium plating.
Questions