Corrosion Properties of Cold-Sprayed Coatings

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Presentation outline

- Cold spraying at TUT
- Denseness improvement
- Corrosion properties of cold-sprayed Ta, Ni, Cu, NiCr, NiCu, NiCr+Al₂O₃, NiCu+Al₂O₃ coatings
- Laser-assisted cold spraying
- Summary
Cold spraying at TUT

Cold spray research
- Focus points: materials, structures, corrosion resistance, functional properties and affecting factors
- International collaboration: e.g., Germany, France, Italy, UK, Spain

Equipment
- High-pressure cold spray system
  Kinetiks 3000 (700°C, 30 bar)
- Kinetiks 4000 in collaboration with Linde (Germany)
- Low-pressure cold spray system
  DYMET 403K (650°C, 9 bar)
- Laser-assisted cold spray
Denseness improvement

1. Optimized powder - spray parameter combination
   - E.g., HPCS Cu, Ta and Ni coatings
   - Powder characteristics → tailored powders
   - Higher preheating temperatures and effectiveness

2. Hard particle addition to densify metallic structures
   - E.g., HPCS NiCr+Al$_2$O$_3$, NiCr+WC-Co-Cr and NiCu+Al$_2$O$_3$ coatings
   - E.g., LPCS Cu+Al$_2$O$_3$ coatings
   - Three functions: 1) Keep the nozzle clean, 2) Activate the sprayed surface and 3) Hammer the coating structure

3. Heat treatments as post-treatments
   - E.g., HPCS Ni and NiCu coatings
Coating materials selected

1. **Ta:** Tantalum has extraordinary corrosion resistance in acids, salts, and organic chemicals even at elevated temperatures

2. **Cu:** Corrosion resistant against e.g., general atmospheric exposure, seawater, waters, dilute sulfuric, phosphoric and acetic acids

3. **Ni:** Pure nickel has excellent resistance to aqueous corrosion, organic salts, alkalines and in particular to caustic soda

4. **NiCu:** Monel alloys has good corrosion resistance in seawater, sulfuric, hydrochloric and hydrofluoric acids

These materials give the anodic protection to steel substrate (coating material is nobler than substrate)

→ Corrosion protection based on passivity (formation of protective layer on the coating surface)

→ Coatings have to be dense and impermeable in order to act as real corrosion barrier coatings
# Cold spray parameters

- Process gas: N\(_2\), coating layers: 2
- Heat-treatments: 600°C, 2 h, in protective atmosphere

## Kinetiks 4000 (HPCS)

<table>
<thead>
<tr>
<th></th>
<th>Ta</th>
<th>Cu</th>
<th>Ni</th>
<th>NiCu</th>
<th>NiCu+Al(_2)O(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature (°C)</strong></td>
<td>800</td>
<td>490</td>
<td>700</td>
<td>650</td>
<td>750</td>
</tr>
<tr>
<td><strong>Pressure (bar)</strong></td>
<td>38</td>
<td>32</td>
<td>40</td>
<td>39</td>
<td>38</td>
</tr>
<tr>
<td><strong>Spray distance (mm)</strong></td>
<td>40</td>
<td>40</td>
<td>50</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td><strong>Beam distance (mm)</strong></td>
<td>1.5</td>
<td>1.5</td>
<td>1</td>
<td>1.5</td>
<td>1</td>
</tr>
<tr>
<td><strong>Traverse speed (m/min)</strong></td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

![Images of Ta, Cu, Ni, NiCu, NiCu+Al\(_2\)O\(_3\)](image)
Denseness improvement
Optimized powder - spray parameter combination

Dense coating structure
- Highly plastically deformed structure
- Metal-metal bonding
- Adiabatic shear instability and material jets
Dense coatings

Impermeable microstructure of HPCS Ni, Cu and Ta coatings → open-cell potential is close to the bulk material behavior
Corrosion properties of HPCS Ta

HPCS Ta coating behaved like corresponding Ta bulk material in 3.5% NaCl and 40% H$_2$SO$_4$ solutions $\rightarrow$ similar corrosion resistance $\rightarrow$ rapid passivation $\rightarrow$ corrosion protection

HPCS Ta coating behaved like corresponding Ta bulk material also in 20% HCl solution, however, passivation was first linear, then curving slightly and followed again linear behavior $\rightarrow$ repassivation

Koivuluoto et al., J. Therm. Spray Technol., 18(1)2009, 75-82
Corrosion properties of HPCS Ta

Nyquist plots: CS Ta has significantly higher values than IPS Ta

Electrochemical impedance spectra:
Applying voltage perturbation amplitude of ±50 mV over frequency range of 100 kHz – 10 mHz (7 points/decade)

<table>
<thead>
<tr>
<th></th>
<th>$R_S$ (Ω)</th>
<th>$R_C$ (Ω)</th>
<th>$R_{CT}$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPS Ta</td>
<td>3.8</td>
<td>36.10</td>
<td>6870</td>
</tr>
<tr>
<td>CS Ta</td>
<td>3.8</td>
<td>2083</td>
<td>674000</td>
</tr>
</tbody>
</table>

IPS coating is more porous $\rightarrow$ lower $R_C$
Pores and weak lamellar boundaries cause extensive electrolyte (1M KOH) penetration

Low $R_{CT}$ $\rightarrow$ system is not behaving as capacitor and charge transfer reaction is going on: part of active dissolution is presumably involving substrate

Very high $R_{CT}$ $\rightarrow$ System is perfectly passive, behaves as capacitor

CS coatings are dense (no through-porosity) $\rightarrow$ much larger $R_C$

Hot corrosion/oxidation test

- 24 x 24 mm samples (low-C steel substrate) were sprayed with ~10 mg/cm² of Na₂SO₄ / NaCl aqueous solution.
- Samples left at 705 °C for 24 h.

Corrosion properties of HPCS Ni

The polarization behavior of as-sprayed and heat-treated HPCS Ni coatings and Ni bulk material

- The polarization behavior of Ni coatings is remarkably close to that of bulk Ni in all solutions → Indicating similar corrosion resistance

Denseness improvement
Hard particle addition

Structure of HPCS Ni20Cr coating
➔ open boundaries

Structure of HPCS Ni20Cr+50Al₂O₃ coating
➔ without noticeable pores
Effect of spray parameters:
Higher preheating temperature

Effect of feedstock:
Hard particle addition
## Corrosion resistance of HPCS NiCu

<table>
<thead>
<tr>
<th>Sample</th>
<th>Test solution</th>
<th>$E_{corr}$ (mV)</th>
<th>$I_{corr}$ ($\mu$A/cm$^2$)</th>
<th>$R_p$ (k$\Omega$cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCu bulk</td>
<td>NaCl</td>
<td>-117</td>
<td>0.766</td>
<td>26.10</td>
</tr>
<tr>
<td>NiCu_Al$_2$O$_3$ (AS)</td>
<td>NaCl</td>
<td>-206</td>
<td>0.711</td>
<td>20.02</td>
</tr>
<tr>
<td>NiCu_Al$_2$O$_3$ (HT)</td>
<td>NaCl</td>
<td>-202</td>
<td>1.35</td>
<td>16.04</td>
</tr>
<tr>
<td>NiCu1(AS)</td>
<td>NaCl</td>
<td>-252</td>
<td>3.35</td>
<td>18.69</td>
</tr>
<tr>
<td>NiCu bulk</td>
<td>H$_2$SO$_4$</td>
<td>21</td>
<td>9.26</td>
<td>1.76</td>
</tr>
<tr>
<td>NiCu_Al$_2$O$_3$ (AS)</td>
<td>H$_2$SO$_4$</td>
<td>20</td>
<td>8.39</td>
<td>1.87</td>
</tr>
<tr>
<td>NiCu_Al$_2$O$_3$ (HT)</td>
<td>H$_2$SO$_4$</td>
<td>17</td>
<td>11.0</td>
<td>1.21</td>
</tr>
<tr>
<td>NiCu1(HT)</td>
<td>H$_2$SO$_4$</td>
<td>21</td>
<td>14.9</td>
<td>0.94</td>
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<tr>
<td>NiCu bulk</td>
<td>HCl</td>
<td>-96</td>
<td>6.69</td>
<td>4.18</td>
</tr>
<tr>
<td>NiCu_Al$_2$O$_3$ (HT)</td>
<td>HCl</td>
<td>-173</td>
<td>5.72</td>
<td>4.83</td>
</tr>
<tr>
<td>NiCu1(HT)</td>
<td>HCl</td>
<td>-193</td>
<td>8.62</td>
<td>2.38</td>
</tr>
</tbody>
</table>

Polarization resistance $R_p$ was calculated by using Stearn-Geary equation ($I_{corr}=B/R_p$)

Corrodkote results: HPCS NiCu

Corrodkote test
- About 100 times more accelerated than salt spray test
- A thick corrosive suspension (copper-nitrate and ferric and ammonium chlorides in a clay water matrix) is uniformly spread on to the surface
- The sample is kept for 80 h (cycles of 20 h) at 38 °C, 85% relative humidity
- Test were done at UNIMORE

Heat-treated sample (HT)
Tighter inter-lamellar boundaries
→ Lower interface corrosion

After 80 h

Corrodkote results: HPCS NiCu+Al$_2$O$_3$

Cavitation erosion wear (ASTM G32)

$$MDE(\mu m) = \frac{10 \Delta W}{\rho A}$$

$$\Delta W = \text{weight loss}$$
$$A = \text{worn area}$$
$$\rho = \text{density of material}$$

$$R_e(h/\mu m) = 1/(\text{SER})$$

SER = steady erosion rate


- Improved deposit qualities
- Higher performance deposits
- Increased corrosion resistance
- Improved cost effectiveness
LACS Ni20Cr coatings

Slow traverse speed, 3 m/min

Improvements with laser:
- Increased coating thickness → Improved DE
- Higher deformation level 100% > 50% > 0%
- Less oxidized particle boundaries 100% < 50% < 0%
LACS Cu10Sn coatings

L0_deF L0_F

L100_deF L100_F

LACS Cu10Sn coatings: less oxidized structures
- Power 0% improvement 100%
- Laser beam in defocus improvement in focus
LACS Cu10Sn coatings

Denseness improvement by using laser-assisted cold spray process (L100_F)

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Summary

- Cold spraying enables the production of fully dense coatings
- Strongly deformed and tightly bonded structures as dominant microstructures → High quality coatings
- Four ways for denseness improvement:
  - Optimized powder – spray parameter combination
  - Addition of hard particles to metallic powder
  - Heat-treatments
  - Laser-assisted cold spraying
- Cold-sprayed Ta coatings have very good corrosion properties: high protectiveness in several environments, gas-tight structure, passivity behavior and excellent passivation stability
- More ductile structure of heat-treated NiCu coatings → Higher cavitation erosion resistance
- Improved corrosion protection and high performance of HPCS Ta, Ni and NiCu coatings → Potential to use as real corrosion barrier coatings!
Thank you for your attention!

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