Development of Low Temperature Spray Process for Manufacturing Fuel Cladding and Surface Modification of Reactor Components

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Project Team

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- Oxford University, UK (Dr. Patrick Grant, unpaid international collaborator)

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Presentation Outline

- Introduction, Motivation, and Project Overview
- Brief Review of Cold Spray Deposition Process
- Development of Cold Spray Process for Oxide Dispersion Strengthened (ODS) Steel
- Cold Spray Manufacturing of ODS Fuel Cladding Tubes
Introduction, Motivation, and Project Overview
Broad Objectives of the Project

Develop **low temperature, solid-state** (*no melting involved*) powder spray deposition process (cold spray process) as a:

- Rapid, near-net shape manufacturing of oxide dispersion strengthened (ODS) steel cladding tubes
- High deposition rate coating technology for corrosion and wear protection, and repair of nuclear reactor components
Oxide Dispersion Strengthened (ODS) Steels

- ODS steels are ferritic (BCC) and contain fine dispersion of nanometer-sized oxide particles (Y-Ti-O) [0.2 to 0.3 wt.%]

- Has the low radiation-induced swelling of conventional ferritic steels

- High temperature strength superior to conventional ferritic steels

- Regarded as a cross-cutting material for multiple reactor concepts

[1] Sridharan et al., UW-Madison
[2] courtesy Dr. Hoelzer, ORNL
Role of Oxide Nanoparticle (nanoclusters) in Ferritic Steels

Increase in High Temperature Strength

Enhanced Radiation Damage Tolerance

Conventional Manufacturing of ODS Cladding Tubes – Slow and Expensive Process

- Melting processes cannot be used as they lead to upward stratification of oxide nanoparticles.
- Milled powders are canned and degassed at 400°C and subjected to multiple hot/warm extrusion steps (8-10 steps) at temperatures > 1000°C and lower temps.
- Low strain rate extrusion processes not conducive to large-scale manufacturing.
- May lead to grain anisotropy, and anisotropy in mechanical properties.

Conventional fabrication of ODS steel tubes requires multiple extrusion steps [3]

Gas atomize ferritic steel powders with Y, Ti, O
Atomization does not fully solutionize Y, Ti, and O therefore ball milling is done with some added FeO to achieve full solutionizing (mechanical alloying)
During high temperature consolidation treatments, oxide nanoclusters come out of solution
Concept of Manufacturing ODS tube via Cold Spray Process

- Three major steps for cold spray manufactured ODS cladding tube

![Diagram showing the process stages](image)

Potential Benefits:

- Eliminates multiple extrusion steps
- May eliminate ball milling mechanical alloying
- Fabrication process faster and cheaper
Key Objectives and Milestones

1. **Optimization** of the powder spray process for the manufacture of ODS cladding tubes

2. Post-deposition **thermo-mechanical treatments**

3. **Characterization and testing** of ODS steel cladding tubes produced by cold spray process

4. **Surface modification and coatings** by cold spray process for addressing corrosion and wear in reactor components, (i) single material coatings, (ii) compositionally-graded coatings, and (iii) multi-layered coatings.

5. **Bench-marking** and **alternative** novel approaches
Brief Overview of Cold Spray Deposition Process
Cold Spray Process

- Powder particles of the coating material propelled at supersonic velocities by a gas onto the surface of a part to form a coating or deposit
- Particle temperature is low – particles are not melted and deposition occurs in solid state
- Coating/deposit formation occurs by particle deformation and an associated adiabatic shear mechanism

Zn cold spray coating on steel substrate
Cold Spray Process – Attributes as a Manufacturing Process

- Performed at ambient temperature
- Performed at atmospheric pressure
- High deposition rates – fast manufacturing
- Supports factory and field fabrication
- High technology readiness level
Cold Spray Laboratory at University of Wisconsin, Madison (est. 2012)

- 4000-34 KINETIK System, from ASB Industries/CGT-GmBH
- Spray booth from Noise Barriers
- Robot controlled (Nachi system, from Antennen)

- Robot for pre-programmed movement of spray gun
- Sample stage and dust collector (below that)
- Sound-proof spray booth
- Nitrogen/helium gas cylinders
- Robot controls (left) and spray gun control (right)
Development of Cold Spray Process for Manufacture of ODS Steel
Feedstock Powder for Cold Spray Process

- Received from Oak Ridge National Laboratory
  - 14YWT (Fe-14Cr-3W-0.4Ti-0.2Y-0.25O)
  - Gas-atomized, spherical powder
  - Size less than 44 µm
  - Large grain size (4 to 8 µm)
Nanoparticles in Feedstock Powder

- Y and Ti-rich nanoparticles in size of 10 nm to 200 nm are dispersed in the ferritic steel matrix

Transmission Electron Microscopy (TEM) lamellae prepared from a particle

TEM images showing fine particles in the matrix
Y and Ti Detection in the Fine Nanoparticles in 14YWT Powder

**HAADF Image**

**EDS spectra**

<table>
<thead>
<tr>
<th>Inside nanoparticle</th>
<th>Outside nanoparticle</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="HAADF Image Inside nanoparticle" /></td>
<td><img src="image2" alt="HAADF Image Outside nanoparticle" /></td>
</tr>
<tr>
<td><img src="image3" alt="EDS spectra Inside nanoparticle" /></td>
<td><img src="image4" alt="EDS spectra Outside nanoparticle" /></td>
</tr>
</tbody>
</table>

**Atomic %**

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Cr</th>
<th>O</th>
<th>W</th>
<th>Ti</th>
<th>Y</th>
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</thead>
<tbody>
<tr>
<td>Inside particle</td>
<td>73.4</td>
<td>11.5</td>
<td>12.0</td>
<td>0.5</td>
<td>too low</td>
<td><strong>2.2</strong></td>
</tr>
<tr>
<td>Outside particle</td>
<td>72.5</td>
<td>15.1</td>
<td>11.9</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
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</table>
Thick and Dense ODS Cold Spray Deposit on Flat Substrates

- 14YWT powder was successfully deposited onto 6061-T6 aluminum flats
- Deposits were very dense with negligible porosity
- XRD confirmed no phase change or oxide inclusions of powder during deposition
Initial Parametric Investigation of Cold Spray Process for Optimal Parameter

Three different gas conditions were investigated

- 100% nitrogen
- Helium/nitrogen mixture A
- Helium/nitrogen mixture B (more helium gas)

Five substrates were investigated

- Annealed 6061
- 6061-T6
- 7075-T6
- Two different cold rolled 6061-T6 substrates
Parametric Investigation of Cold Spray Process (Propellant Gas and Substrate Effect)

<table>
<thead>
<tr>
<th>100% N₂</th>
<th>Annealed 6061</th>
<th>6061-T6</th>
<th>40% CR 6061-T6</th>
<th>80% CR 6061-T6</th>
<th>7075-T6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixture B</td>
<td></td>
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</table>

Hardness range of substrates from 60HV – 170HV
- No significant affect seen from cold spray process in terms of deposition thickness
  - Showed the least amount of porosity

Optimal cold spray parameter set with 6061-T6 substrate because it is readily available and can be easily dissolved
Further Parametric Investigation of Cold Spray Process (powder size effect)

- Two different powder size distributions investigated:
  - 25-44 µm size powder
  - -44 um size powder that included powder sizes less than 25 um
- The -44 um sized powder increased both the deposit density and thickness
Why is there an increase in deposition thickness and density?

Sprays with 25-44 µm powder

- Smaller particle sizes were able to deform more readily (higher velocity) and could deposit and fill in pores between the larger particles increasing the deposit thickness and decreasing the porosity.

Sprays including less than 25 µm powder

< 25 µm
Microstructure of as-deposited 14YWT

FIB lift-out technique

Grain refinement (grain size is less than 1µm)

High density of line dislocations in the small grains

Dislocation forest and disappearance of the nanoparticles
Dissolution of Aluminum Mandrel

• Dissolution studies on both 6061-T6 and 7075-T6 aluminum flats were performed in 20% NaOH solution

• 6061-T6 dissolved faster than 7075-T6

• Of course, stirring increased dissolution rate
Post-heat Treatment of ODS Flats/Tubes

- Annealing experiments were conducted for precipitation the Y-Ti-O nanoclusters and improve ductility
- Flats/Tubes were annealed in a quartz tube furnace at 800°C, 900°C, 1000 °C and 1100 °C for 1 hour
Microstructural Evolution during Post-heat Treatment (SEM Images & Hardness)

As-deposited

![SEM Image]

- Grain growth with increasing annealing temperature
- Annealing studies were performed on un-optimized ODS tube deposit

Done on un-optimized microstructure (porosity in the matrix, which has now been now addressed)

- 800°C
- 900°C
- 1000°C
- 1100°C

Hardness (HV/0.05) vs Annealing Temperature (°C)
Microstructural Evolution during Post-heat Treatment (TEM Images)

- The heat treatment (1000 °C) induced strain relaxation, recrystallization, and reprecipitation of nanoparticles or nanoclusters.

Nanoparticle dispersed in the grain
Annealed out dislocation forest
Fine nano-particles (~ 40 nm)
Chemical Composition of Nanoparticles in Heat Treated ODS Deposit

HAADF Images

Ti and Y-rich and low oxygen particle

EDS line profile

Ti-rich and high oxygen particle
Cold Spray Manufactured ODS Fuel Cladding Tubes
Step 1: ODS Cladding Tube Fabrication: Cold Spray Deposition

- Deposition was performed on a 6061-T6 aluminum tube mandrel (0.375” OD) while rotating
- Cold spray parameters were adjusted to achieve the highest quality deposit using 4” long tubes
- A longer 10” tube was then produced to show scalability for full length cladding tube
Deposition of ODS on 6061-T6 Aluminum Tube Mandrel

5” tube formed in ~ 60 seconds
Thickness: 1 mm for < 44 μm size particles
Step 2: Dissolution of Aluminum Tube Mandrel to leave free-standing ODS Tube

- Dissolution of the aluminum tube mandrel in 20% NaOH solution
- Final polishing of the ODS cladding tube was done to improve surface finish
Step 3: Vacuum Heat Treatment of ODS Tube

- Tubes were vacuum heat treated at 1085°C for 1 hour to eliminate all residual porosity in the cladding tube.
- Vacuum heat treatment serves to both precipitate oxide nanoclusters and promote densification.

Vacuum heat treatment performed at Thermal Spray Technologies (TST)
Final Free-Standing ODS Cladding Tube

8” ODS cladding tube
Immediate Future Work

- Further optimization of the manufacturing process including microstructural engineering (e.g., grain size, nanocluster size/density)
- Mechanical testing of ODS cladding tubes
- Heavy ion irradiation experiments on ODS cladding tubes
- Seeking future opportunities for neutron irradiation experiments and associated post-irradiation examination research (not a part of NEET program)
- Surface modification and coatings for corrosion and wear resistance (e.g., multi-layered coating and compositionally graded coatings)

Dual-layered (FeCrAl and Mo) coating on Zr-alloy

IN600 coating on steel
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