Thermal Spray Coatings in Severe Service

Elaine Motyka
3/2/2017
In this session

• **Basics of Thermal Spray Coatings**
  • Defining Thermal Spray
  • Common processes
  • Coating microstructures
  • Properties affected by process and structure
  • Application considerations

• **Severe Service for Thermal Spray Coatings**
  • Defining severe service
  • Coating factors affecting wear and corrosion
  • Two specific coatings for wear and corrosion
  • Fusing, blending, and graded structures
  • Example: ASTM G65 wear performance
Basics of Thermal Spray

The materials engineering paradigm applies to thermal spray coatings

Structure

Performance

Processing

Properties

 Privileged and Confidential
Basics of Thermal Spray

• Defining Thermal Spray
  • Deposition of layers of fine particulate material using thermal and kinetic energy onto a prepared substrate.
    - From tens of microns up to millimeters (2 to 200+ mils) thick.
    - Rapid process.
    - Wide range of thicknesses and compositions for engineered properties and performance.
    - Many different types of “guns”/process equipment exist for thermal spray deposition.
Basics of Thermal Spray

- Common commercial processes

Diagram:
- Thermal Spray Processes
  - Using electric discharge
    - Wire arcspray
  - Using plasma energy
    - Plasma spray at 1 atm, in air or shrouded
  - Using expansion of gases (no combustion)
    - Plasma spray under vacuum
    - Low pressure in chamber
    - Cold spray
  - Using combustion (gaseous or liquid fuel)
    - D-gun
    - Flame spray (powder or wire)
  - Using laser energy
    - HVOF
Basics of Thermal Spray

• Process-specific temperature & velocity
Basics of Thermal Spray

• Flame spray
  • Low propelling gas velocity
    - Lower bond & higher porosity
    - Higher oxidation of particles
    - Higher quenching/tensile residual stress

• HVOF
  • High propelling gas velocity, >Mach-1
    - Higher bond & lower porosity
    - Lower oxidation of particles
    - Higher peening/compressive residual stress
Basics of Thermal Spray

- Coating microstructure features: as-deposited

- Many of these can be changed by post-deposition processes such as thermal treatments....
Basics of Thermal Spray

- Large number of process and material factors affect the part performance

- **Feedstock characteristics**
  - Composition
  - Size distribution
  - Morphology
  - Density

- **Process factors**
  - Spray plume orientation
  - Particle distribution
  - Particle temp & velocity

- **Deposition rate factors**
  - Powder feedrate
  - Part rotation speed
  - Gun raster speed & step
  - Gun angle

- **Substrate characteristics**
  - Part geometry
  - Composition
  - Temperature
  - Roughness
  - Cleanliness

- **Coating structure**
  - Defects (cracks, pores, oxides, unmelts)
  - Phases and compositions
  - Splat characteristics
  - Grain size

- **Coating properties**
  - Mechanical (YS, E, residual stress)
  - Physical (thermal conductivity, dielectric, density)
  - Functional (wear resistance, corrosion)

- **Part performance**
## Basics of Thermal Spray

- A very few common thermal spray coatings

<table>
<thead>
<tr>
<th>Coating Family</th>
<th>Nomenclature</th>
<th>Composition</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metallics</strong></td>
<td>Ni-5Al</td>
<td>95%Ni-5%Al</td>
<td>Dimensional restoration, Bond coating, corrosion</td>
</tr>
<tr>
<td></td>
<td>NiCrFeNbTaMoTi</td>
<td>Inconel 718</td>
<td>High-temp oxidation and corrosion to 1800F, repair</td>
</tr>
<tr>
<td></td>
<td>Al-12Si</td>
<td>88%Al - 12%Si</td>
<td>Dimensional restoration, traction, anodic protection</td>
</tr>
<tr>
<td></td>
<td>FeCrNiMo</td>
<td>316 stainless steel</td>
<td>Corrosion, cavitation, fretting, erosion, dim. rest.</td>
</tr>
<tr>
<td></td>
<td>NiCrBSiFe</td>
<td>Ni 7.0-16.5Cr 4.5Fe 4.0-4.5Si 3.0-3.25B (Similar to braze compounds)</td>
<td>Self-fluxing alloy, corrosion &amp; wear up to 1500F</td>
</tr>
<tr>
<td><strong>Cermets/Carbides</strong></td>
<td>Cr3C2-NiCr</td>
<td>75%Cr3C2-25%NiCr</td>
<td>High-temp cavitation &amp; wear, hot gas corrosion to 1600F</td>
</tr>
<tr>
<td></td>
<td>WC-CoCr</td>
<td>86%WC – (10%Cr 4%Co)</td>
<td>Low-temp wear to 900F</td>
</tr>
<tr>
<td></td>
<td>WC-12Co-Ni S/F</td>
<td>50%(WC-12Co)-50%NiCrBSiFe</td>
<td>Wear, impact, up to 900F</td>
</tr>
<tr>
<td><strong>Ceramics</strong></td>
<td>Al2O3</td>
<td>99% Al2O3</td>
<td>Wear, alkali/acid resistance, dielectric</td>
</tr>
<tr>
<td></td>
<td>Al2O3- 40TiO2</td>
<td>60%Al2O3 – 40%TiO2</td>
<td>Wear, alkali/acid resistance, dielectric</td>
</tr>
<tr>
<td></td>
<td>Cr2O3</td>
<td>99% min. Cr2O3</td>
<td>Wear and chemical resistance up to 1000F</td>
</tr>
<tr>
<td></td>
<td>ZrO2-8Y2O3</td>
<td>92% ZrO2 – 8% Y2O3</td>
<td>Thermal barrier</td>
</tr>
</tbody>
</table>
Severe Service for Thermal Spray Coatings

Considerations for using thermal spray coatings

- **Advantages**
  - Does not heat the substrate significantly so it won’t distort the part or affect substrate properties or heat treated condition
  - A very large variety of materials can be deposited, many which can be customized by blending or grading
  - High deposition rates compared to plating or thin film processes
  - Relatively thick coatings, .005” to >.050”, for aggressive applications
  - HVOF has no negative effect on fatigue life
  - Wide range of applications: wear, corrosion, thermal and electrical conductivity, traction, etc.
  - Non-fused coatings can be stripped by chemical or mechanical means
Severe Service for Thermal Spray Coatings

Considerations for using thermal spray coatings

• Disadvantages

  • Line-of-sight process; must be able to “see” the area to be coated. Can spray at non-90deg angles to reach into small diameters in some cases
  • Not metallurgically bonded as-deposited, but can be heat treated to do so in some cases
  • Validation testing recommended where bending stress or point loading is high or where elastic strain of the substrate is high or CTE mismatch is high
  • All coatings have some level of porosity, typically 1-5% for HVOF, unless fused/sintered by heat treating or sealed
  • Requires machining or grinding to achieve fine finishes; after finishing <16μin typical
Thermal Spray Coatings in Severe Service

• Severe service defined for coatings
  • Aggressive wear, corrosion, wear & corrosion, thermal shock, high temperature/pressure, impact, high strain, fatigue, etc.

• For valves, severe wear and corrosion mechanisms
  • Wear Mechanisms
    - Abrasion
    - Erosion
    - Fretting
    - Sliding
  • Corrosion Mechanisms
    - General
    - Galvanic
    - Localized
    - High temperature oxidation

• Two coatings for wear and corrosion service
  • Both composite materials: hard phases in a softer tougher matrix
    - Carbide cermet
    - Fused/sintered metallic
Thermal Spray Coatings in Severe Service

- **Coating Factors Affecting Wear**
  - Hardness
  - High elastic modulus
  - High toughness
    - High hardness with insufficient toughness: possible brittle fracture and delamination
  - Good adhesion
  - Thickness
    - Must be sufficient to distribute the stresses from localized loading from the surface to the base metal
    - Insufficient thickness under localized loading: possible eggshell effect
Thermal Spray Coatings in Severe Service

• **Coating Attributes Affecting Corrosion**
  - Thermal spray coatings have porosity and oxides
    - Pathways for corrosive media
    - Less noble or less likely to passivate
  - Cathodic type protective coatings for severe service
    - Must minimize as-sprayed oxides and pores
      - HVOF process
    - Minimize remaining pores, post-spraying
      - Sealants
        - Organic (epoxies, silicones, etc.)
        - Inorganic (silicates, etc.)
      - Densification
        - HVOF provides the most dense as-deposited coatings
        - Chemical treatments
        - Thermal treatment as post-deposition process; sinter or fuse
Thermal Spray Coatings in Severe Service

- Coating alternatives for wear & corrosion
  - Combine hardness and toughness
    - Composite with hard phases in a tougher metal matrix
  - Low porosity and oxides, high bond and load capacity
    - HVOF process

Cermets of WC-CoCr or Cr3C2-NiCr

NiBSi metallic alloys of NiCrFeSiB or NiCrWFesiB
Thermal Spray Coatings in Severe Service

• Carbide Cermets
  • Carbide phase in metallic matrix (e.g., WC-CoCr & Cr3C2-NiCr)
    - Higher %carbide increases hardness but reduces toughness
    - Control carbide size relative to abrasive size
    - Hardness vs angle of impingement for erosion

• Typical data for WC-Co cemented carbides:

  ![Diagram showing hardness vs Co-content and fracture toughness vs Co-content.](image)

  - Finer carbides, lower %metal matrix
  - Higher %carbide increases hardness but reduces toughness
  - Control carbide size relative to abrasive size
  - Hardness vs angle of impingement for erosion
Thermal Spray Coatings in Severe Service

• Carbide Cermets
  • Composition of matrix (Co, CoCr, Ni, NiCr)
    - During spraying
      o Carbide dissolution, WC->W2C, W
      o Matrix oxidation, loss of Cr
    - CoCr and NiCr matrix more corrosion resistant than Co
      o Cr allows passivation
    - Carbide type has some effect also
  • WC for lower temperature applications; Cr3C2 for higher temperatures (oxidation)
  • Sealants recommended

• Tribo-Corrosion
  • Wear dominant
  • Corrosion dominant
Severe Service for Thermal Spray Coatings

- **Ni-B-Si metallic alloys**: NiCrFeSiB, NiCrWFeSiB, etc.
  - HVOF vs flame spray as-deposited, note pores & grain size & homogeneity
 Thermal Spray Coatings in Severe Service

- **Ni-B-Si metallic alloys:** NiCrFeSiB, NiCrWFeSiB, etc.
  - Historically sprayed by flame spray process then fused
    - High porosity, low bond as-sprayed
    - Greater shrinkage during post-spray fusing
    - Risk of cracking and incomplete closing of pores
    - HVOF coatings shown here
- Many compositions, similar to braze alloys
  - Eutectic allows fusing at lower temperature than individual phases
Thermal Spray Coatings in Severe Service

- **Ni-B-Si coatings: the constituents**
  - Boron and Silicon
    - lower the melting range
    - provide fluxing properties to allow the coating to be fused and metallurgically bonded
    - particularly Boron is hardens the coating forming Cr- & W- Boride phases
  - Iron and Carbon
    - improve the wetting properties of the alloy above its solidus temperature.
  - Chromium
    - widens the range between solidus and liquidus temperatures and alters the atomic structure so that a face centered cubic (austenitic type, non-magnetic) structure is achieved.
    - provides for the formation of a protective chrome-oxide surface layer
    - Increases wear resistance by formation of Chromium carbides.
  - Tungsten
    - in solid solution with Nickel it increases the coatings high temperature strength and provides resistance to localized corrosion (known as pitting)
    - also a carbide former
      - increase wear resistance due to the higher hardness of tungsten carbide versus chrome carbide
      - tie up some of the Carbon that would otherwise form chrome carbide so that more Chromium is left in the solid solution to enhance the corrosion resistance of the coating.
Thermal Spray Coatings in Severe Service

- **Ni-B-Si metallic alloys**: NiCrFeSiB, NiCrWFeSiB, etc.
  - As-deposited phases:
    - NiCr gamma-phase & Cr3B2 intermetallic
    - Mechanical bond with the substrate
  - Fused or sintered phases:
    - Interdiffusion
    - NiCr-rich matrix with Cr-, W- carbides, borides, silicides that are harder than the matrix
    - Metallurgical bond
    - Graded structure
      - Load carrying capacity
      - Graded mechanical and physical properties
        » Modulus, YS
        » CTE
Thermal Spray Coatings in Severe Service

• Post-processing by fusing or sintering
  • Torch fusing in air
    - Surface heating in air
    - Manual operation
  • Furnace sintering in vacuum / inert gas
    - Batch-process
    - Controlled ramp, soak, cooling and atmosphere
    - Heats entire part
  • Induction fusing
    - Surface heating, more localized
    - Controlled, faster heating and cooling
  • Others...

• Temperature range between solidus and liquidus can be large
  - Coating flow/creep
  - Dilution with substrate
  - Phase formation (thermodynamics vs kinetics)
Thermal Spray Coatings in Severe Service

- **Ni-B-Si coating microstructure features:** fused/sintered
  - Coating densification and diffusion near the solidus
  - Sintering time/temperature allow for pore closure within the coating
  - and for diffusion of coating elements into the substrate
  - Longer fusing time or temperature increases dilution with the coating-substrate interface
    - may reduce hardness of the coating
    - but may provide a graded structure that is more tolerant of thermal shock and impact.

**NiCrWFeBSi as-deposited**

- Increasing fuse temp
  - Sample Tab
  - bench oven
  - air
  - Soak 1860°F, 30min.
  - 811HV

- Soak 1900°F, 30min.
  - 777HV

- Soak 1940°F, 30min.
  - 761HV
Thermal Spray Coatings in Severe Service

- Sintered Cr3C2-NiCr (25% binder)
  - Decrease in hardness, 874 to 640 HV
  - Slight reduction in porosity
  - Slight diffusion with substrate
Thermal Spray Coatings in Severe Service

- **Blending WC-Co and Ni-Si-B alloy**
  - 50wt% blend is typical
  - Additions as low as 10wt% WC-Co have wear advantages
  - Tribo-corrosion applications -> harder and fusible
  - Additional hard phase and/or matrix strengthening

- **WC dissolution during sintering**
  - Matrix strengthening
  - Homogeneous
  - Graded (load carrying capacity, bond)
  - Lower hardness

<table>
<thead>
<tr>
<th>as-deposited</th>
<th>increasing fuse time</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>842 HV</td>
<td>1108 HV</td>
<td>1074 HV</td>
<td>799 HV</td>
<td></td>
</tr>
</tbody>
</table>
Thermal Spray Coatings in Severe Service

- Effect of coating composition, microstructure, processing on 3-body dry-sand abrasive wear
THE TECHNICAL DATA CONTAINED HEREIN IS BY WAY OF EXAMPLE AND SHOULD NOT BE RELIED ON FOR ANY SPECIFIC APPLICATION. TECHNETICS GROUP WILL BE PLEASED TO PROVIDE SPECIFIC TECHNICAL DATA OR SPECIFICATIONS WITH RESPECT TO ANY CUSTOMER’S PARTICULAR APPLICATIONS. USE OF THE TECHNICAL DATA OR SPECIFICATIONS CONTAINED HEREIN WITHOUT THE EXPRESS WRITTEN APPROVAL OF TECHNETICS GROUP IS AT USER’S RISK AND TECHNETICS GROUP EXPRESSLY DISCLAIMS RESPONSIBILITY FOR SUCH USE AND THE SITUATIONS WHICH MAY RESULT THEREFROM.

TECHNETICS GROUP MAKES NO WARRANTY, EXPRESS OR IMPLIED, THAT UTILIZATION OF THE TECHNOLOGY OR PRODUCTS DISCLOSED HEREIN WILL NOT INFRINGE ANY INDUSTRIAL OR INTELLECTUAL PROPERTY RIGHTS OF THIRD PARTIES.

TECHNETICS GROUP IS CONSTANTLY INVOLVED IN ENGINEERING AND DEVELOPMENT. ACCORDINGLY, TECHNETICS GROUP RESERVES THE RIGHT TO MODIFY, AT ANY TIME, THE TECHNOLOGY AND PRODUCT SPECIFICATIONS CONTAINED HEREIN.

ALL TECHNICAL DATA, SPECIFICATIONS AND OTHER INFORMATION CONTAINED HEREIN IS DEEMED TO BE THE PROPRIETARY INTELLECTUAL PROPERTY OF TECHNETICS GROUP. NO Reproduction, copy or use thereof may be made without the express written consent of TECHNETICS GROUP.