Powder Metal: The Foundation for Metal Additive Manufacturing

John L.L. Meyer
Technical Manager – Carpenter Powder Products
Outline

Intro to Carpenter Technology Corporation / Carpenter Powder Products / CalRAM

Powder 101
- How is powder commonly produced for AM

Main Powder Characteristics and Basic Requirements for AM
- What is important?

Common AM Alloys/Applications

Additional considerations
- Guide procurement of powder
- Avoid ‘rookie’ mistakes/pitfalls
Carpenter: Quick Facts

125+ years of innovation in specialty alloys
$1.8B sales (2017)

Global sales presence

6 product forms

1. Powder
2. Wire
3. AM Solutions
4. Ingot / billet
5. Strip
6. Bar

7 strategic markets

Transportation
Aerospace
Defense
Industrial
Consumer
Medical
Energy

Relationships with major OEMs

Top Aero manufacturers
Medical implant manufacturers
Major industrial and consumer companies
... and hundreds of other OEMs and suppliers across our markets

260+ high performance alloy grades
...and custom compositions available
Global Powder Manufacturing Footprint

Nine atomizers across six locations

- **NORTH AMERICA**
  - Bruceton Mills, WV
    - Titanium EIGA
  - Athens, AL
    - Superalloy VIM
    - Powder manufacturing
    - Regional distribution offices

- **CENTRAL & SOUTH AMERICA**
  - **EUROPE**
    - Woonsocket, RI
      - Ultrafine powder VIM
    - Reading, PA
      - R&D VIM (quick turn-around)

- **ASIA / APAC**
  - Torshalla, Sweden
    - Tool Steel Air Melt

- Bridgeville, PA
  - Vacuum and Air Melt capabilities

VIM = Vacuum Induction Melt
EIGA = Electrode Induction Melt Gas Atomization
### Comprehensive AM Powder Portfolio

<table>
<thead>
<tr>
<th>Element</th>
<th>Alloy Type</th>
<th>Grades and Alloys</th>
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</thead>
<tbody>
<tr>
<td>Ti</td>
<td>Titanium alloys</td>
<td>Puris 5+, Ti-6-4 Gd.5, Ti-6-4 Gd.23, Ti6242, Nitinol</td>
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<tr>
<td>Ti</td>
<td>Gamma-Titanium alloys</td>
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<td>Al</td>
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<td>Ni</td>
<td>Duplex and super duplex SS</td>
<td>2205, 2505, 2507</td>
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<td>W</td>
<td>Nitrogen strengthened SS</td>
<td>BioDur® 108</td>
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<td>C</td>
<td>Martensitic SS</td>
<td>420, 420 Modified</td>
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<td>Controlled thermal expansion</td>
<td>Invar 36, SuperInvar 32-5, Kovar</td>
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<td>Cr</td>
<td>Low alloy stainless steel</td>
<td>4140, 4340</td>
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<td>W</td>
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<td>H13</td>
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<td>Ni</td>
<td>Magnetic alloys</td>
<td>Hiperco® 50</td>
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<td>Cu</td>
<td>Copper alloys</td>
<td>C18200, GrCop-84</td>
</tr>
<tr>
<td>Zr</td>
<td>Zirconium alloys</td>
<td>Zr-702</td>
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</tbody>
</table>

- 50+ years of powder production
- World’s largest producer of gas atomized, pre-alloyed specialty powder metal products
Currently twelve AM machines from six machine OEMs – Binder Jet, L-PBF, EB-PBF, DED (Powder)
Powder for AM - Production

Composition
- **Pre-alloyed** – Each powder particle is homogenous representation of desired bulk chemistry

Powder Production Types – many general types with many variants within a type
- Mechanical (Grinding / Milling)
- Chemical Reduction
- Centrifugal
- Rotating Electrode
- **Atomization (Gas, Water, Plasma Wire)**

<table>
<thead>
<tr>
<th>Technique</th>
<th>Mass median particle size $d_{50} , (\mu m)$</th>
<th>Production rate (kg/min)</th>
<th>$\sigma_{LN}$ (spread)</th>
<th>Energy Efficiency (kWh/ton)</th>
<th>Flow/Spreadability/Chemistry Suitable for AM?</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fine &lt; 50</td>
<td>Medium 50 - 200</td>
<td>Coarse &gt; 200</td>
<td>Low 1 - 10</td>
<td>Medium 10 - 100</td>
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<tr>
<td>Free-Fall Gas Atomization</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
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<tr>
<td>Close Coupled Gas Atom.</td>
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<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
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<tr>
<td>Plasma Wire Atomization</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
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<tr>
<td>Soluble Gas Atomization</td>
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<td>✓</td>
<td>✓</td>
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<td>✓</td>
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<tr>
<td>Water Atomization (sym)</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
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<tr>
<td>REP/ PREP</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
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<tr>
<td>Centrifugal / RSR</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
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<tr>
<td>Hydride-dehydride (HDH)*</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

*Single-step (no gas), *Without post-processing such as plasma spheroidization

Plasma Wire Atomization

1998 – 2004  Pyrogenesis / Raymor JV
2004 – 2006  AP&C operated
    2006  Purchased by AP&C
    2014  Acquired by Arcam AB
    2016  Majority stake acquired by GE
    2017  Pyrogenesis announces entrance to AM powder production market

3.2 mm wire input (2.54 – 3.81 mm), Three 65 kW plasma torches @ Mach 3-4

Highly spherical w/ low satellites
High material efficiency
Can handle high melting / refractory metals
Low throughput (5 kg/hr)
High energy consumption (benefits from cheap Canadian hydroelectric energy)
Limited to metals that can be drawn into wire
- Limits flexibility for alloy customization as dependent on wire lot MOQ
Typically only used for production of Ti grades for EB-PBF, L-PBF
Gas Atomization

Few atomizers are built alike – vary in:

- Air vs. Inert Gas vs. Vacuum Melt (cleanliness)
- Energy source for melting (induction/plasma)
- Refractory materials
- Method of melt introduction (cleanliness)
  - Ceramic-free
  - Top pour vs. bottom pour
- Atomization direction (up/down/horizontal)
- Gas manifold (yield, morphology, flow)
  - Free-fall vs. close-coupled
  - Pour tube geometry
  - Annular vs. discrete jets
  - Convergent vs. convergent-divergent
- Atomization chamber design (morphology, flow)
  - Gas flow dynamics
  - Gas-exhaust / powder collection
  - Heat removal from collected powder
- Atomization Gas (Argon vs. Nitrogen vs. Air)
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Spherical w/ low satellites

**Flexibility in raw materials**
- Allows customization
- Lower cost charge materials (than plasma)

**Low oxygen** (relative to water atomized)

Conventional gas atomization limited by operating temperature of refractories; high melting / refractory metals are challenging

Courtesy: USDOE Ames Laboratory
Powder Characteristics - Morphology

Primary affect of morphology on AM is on flow and spreading characteristics:

- Tendency to jam in powder feeding or cause streaks during spreading
  - Primarily for extremely satellited, flakey, or irregular powder (such as water atomized)
  - Some AM machines are more sensitive to these issues than others

Visual examination (e.g. scanning electron microscopy) alone is insufficient for determining fitness for use in AM process

- No calibrated eyeball / not a beauty contest
- Limited by sampling / low sample size and human error/bias

Sphericity measurements are more useful but morphology is only part of the puzzle
Powder Size – Histograms and Probability

Particle size important impact on:
- chemistry (O -> toughness, etc.)
- particle packing (fill density, flowability/spreadability, surface finish, shrinkage)
- re-meltability - Laser (or Plasma) can only melt up to a certain size particle
- maximum defect size for lifting considerations (below limit of detection)
- Vaporization - build-up on optics or torch tip

Histogram – Graphical representation of frequency by category or bin
Bin – Interval or boundary by which to sort

Particle Size Distribution (PSD)
- Displays amount of powder (frequency) of a given size range (i.e. within a given bin)
Cumulative weight below a particle diameter/size (rather than weight or frequency in a certain size range)

Sometimes powder is specified a tolerance (in µm) on d10, d50, and/or d90

• This is a flawed approach to specifying powder (more later)
Powder size and attributes must be tailored for the powder application.
Powder Sizing – Sieving vs. Air Classification

Mesh # = Openings per inch
- Actual opening is dependent on wire diameter (ASTM E2016)

Particles sorted by what **AREA** they pass through
- Needles with high aspect ratio can fall through even though one dimension is longer

Output tested/certified per ASTM B214 and ASTM E11

Screens with small openings (below ~45 µm) blind (clog) with fine powder rendering them impractical for production processes, another method is needed

Coarse particles
- Large mass = high momentum
- Small surface area:volume = low drag
- **Cannot** be captured in counter air-flow

Particles sorted by aerodynamics
- Balance of outward momentum and inward drag

Output tested/certified per ASTM B822 – laser diffraction
Powder Size Analysis – Test Method Comparison

ASTM B214 – “Stack of Screens” for ≥45 µm
Measures weight passing

Tolerances by wt%

E.g. 5.0% max +140M, 5.0% -325M

ASTM B822 – Laser Diffraction for <45 µm
Uses algorithm to convert diffraction pattern to linear dimension (powder diameter) and then number density to vol% assuming a powder shape (next slide)

Tolerances by vol% = wt%

E.g. 5.0% max -15.63 µm
Particle Size Discrepancies – Morphology and Sieve Tolerances

**Morphology / Shape**

- Discrepancy between laser measurement systems (i.e. Microtrac) and sieve analysis for all but perfect spheres
  - Laser systems require an assumed particle shape or aspect ratio
- Particles to right would all pass through the same sieve opening but laser diffraction could measure the particle size significantly different depending on the orientation as it passes in front of the laser

**Sieves are certified to average opening ASTM E11**

- -325M is nominal average opening of 45 µm
  - Average opening is ± 2.8 µm (41.2 µm – 47.8 µm)
  - Maximum individual allowed opening is + 20 µm
    - 45 µm sieves are allowed to have openings up to 65 µm!
- Tolerances on screens can lead to large discrepancies vs. laser

- Sieve analysis and laser diffraction results are not comparable.
Particle Size Distribution – Specification Guidance

For PSD tolerances CPP prefers:
• sieve analysis for ≥45 µm (+325M) as it is in line with screening process measurement, and
• laser analysis for <45 µm as laser diffraction is used to tune air classification process.

While d10/d90 is appropriate for MIM and some binder jet cuts using d10/d50/d90 for L-PBF/EB-PBF/DED is a flawed approach:
• Three constraints with only 1 degree of freedom
• d90 is indirect measure of industry standard sieving operation and is hindered by low sample statistics (few grams vs. 100g for sieve analysis) and assumed sphericity
• P2P correlations between different instrument manufacturers (Microtrac, Malvern, Horriba, Cilas) are not well established; results between manufacturers or even between models within a manufacturer, may not be comparable.
  • Sieve analysis is universal world-wide.
• Don’t fall into thinking that more decimal points and a digital test report is more accurate or comprehensive
Powder Characteristics - Flow

Hall Flow per ASTM B213
- Good flowability = good AM spreadability, useful for some surface enhancement processes
- Low/no flow ≠ poor AM spreadability

Carney Flow per ASTM B964 or Gustavsson Flow per ISO 13517
- Applicable for powder non-flowing per B213
- Gaining more acceptance

Rheological testing (such as Freeman FT-4) gives better discrimination
- Expensive machine
- Development of correlation between data and real world AM performance yet to be proven

In General:
- Larger and narrower size ranges flow better
- Fine powders may flow worse or not at all.
- Smooth/Spherical powder flows better than irregular powder
## Common Alloys and Applications

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<tr>
<th>Alloy Family</th>
<th>Example Alloys</th>
<th>Example Applications</th>
</tr>
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<td><strong>Puris 5</strong>, Ti-6-4 Gd.5, Ti-6-4 Gd.23, Ti6242, Nitinol</td>
<td>Implants, prosthesis</td>
</tr>
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<td>Gamma-Titanium alloys</td>
<td>TiAl</td>
<td>LPT blades</td>
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<td>Impellers, diffusers</td>
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<td>Fuel nozzle, dental implant</td>
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<td><strong>17-4PH, 15-5PH, Custom 465</strong></td>
<td>Medical instruments</td>
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<tr>
<td>Tool steel</td>
<td><strong>H13</strong></td>
<td>Al die-casting molds</td>
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<td>Magnetic alloys</td>
<td>Hiperco® 50</td>
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<td>Copper alloys</td>
<td>C18200, GrCop-84</td>
<td>Conformal cooled rockets</td>
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Economics of AM Parts & Powder

- **Trade-off of throughput (lb/hr) and resolution**
- **Buy-to-fly**
- **Post-processing (HIP)**
  - PSD tailored to AM machine which determines yield
  - Atomization gas nitrogen vs. argon
  - Tighter/custom composition ranges
- **Additional testing**
- **Special packaging**
- **Order quantity**

**Binder Jet** (small parts)
- Small, accurate shapes
- Prototyping
- Low-volume parts for Consumer devices
- “Desktop” versions

**Laser – Powder Bed Fusion**
- High density, high strength
- Most common
- Aerospace parts
- Medical/dental implants
- Advanced tooling

**Electron Beam – Powder Bed Fusion**
- High density, high strength
- Aerospace parts
- Medical/dental implants

**Binder Jet** (large parts)
- Porous parts (50%)
- Indirect molds for Automotive
- Bronze-infiltrated ornamental pieces
- Future → large valves
- Requires HIP

**Powder (DED¹)**
- Net shape structures, less design freedom
- Aerostructures
- Add detail to pre-forged components
- Repair and overhaul

**Wire feedstock**

1) DED = Direct Energy Deposition
AM Procurement Considerations - Chemistry

Wrought 625 (AMS 5666)

<table>
<thead>
<tr>
<th>Element</th>
<th>Range</th>
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<tbody>
<tr>
<td>Al</td>
<td>0 - .40</td>
</tr>
<tr>
<td>C</td>
<td>0 - .10</td>
</tr>
<tr>
<td>Nb</td>
<td>3.15 - 4.15</td>
</tr>
<tr>
<td>Co</td>
<td>0 - 1.00</td>
</tr>
<tr>
<td>Cr</td>
<td>20.00 - 23.00</td>
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<tr>
<td>Fe</td>
<td>0 - 5.00</td>
</tr>
<tr>
<td>Ta</td>
<td>0 - 0.05</td>
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<tr>
<td>Mn</td>
<td>0 - .50</td>
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<td>Mo</td>
<td>8.00 - 10.00</td>
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<tr>
<td>Ni</td>
<td>Bal</td>
</tr>
<tr>
<td>P</td>
<td>0 - .015</td>
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<tr>
<td>S</td>
<td>0 - .015</td>
</tr>
<tr>
<td>Si</td>
<td>0 - .50</td>
</tr>
<tr>
<td>Ti</td>
<td>0 - .40</td>
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</tbody>
</table>

Missing Elements

- Oxygen
- Nitrogen

Target Aim – Major Elements

- Nb, Cr, Mo

What about residuals

- Al, B, C, Ca, Co, Fe, Mn, P, S, Si, Ti

Wrought to AM Transition Pitfalls to Avoid

- Assuming that cold-worked / wrought alloy properties are achievable via additive (e.g. MP35N vs 625 PLUS – not worth the premium for 35% Co when cold-work can’t be introduced)
- Assuming that interstitial values (e.g. O and N) are achievable in powder (remember O vs. surface area)
- Not considering anisotropic properties
AM Procurement Considerations – PSD / Morphology

Has impact on
- Spreadability/flowability
- Apparent density
  - Resulting influence on part density/defects

Not enough to define desired “rough” cut (e.g. +15 µm, -325 mesh (45 µm))
- Some amount of fines desired to:
  - improve density and surface finish
  - initiate melt pool conduction
- Too many fines:
  - negatively impacts spreadability/flowability
  - increases oxygen content
- Important to define appropriate specifications
  - Restricting oversize and undersize leads to higher costs

<table>
<thead>
<tr>
<th>Size</th>
<th>Allowance wt% (max)</th>
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</thead>
<tbody>
<tr>
<td>+230 (63µm)</td>
<td>0.0, 0.1, 0.2</td>
</tr>
<tr>
<td>+270 (53µm)</td>
<td>0.0, 0.1, 0.2, 1, 3</td>
</tr>
<tr>
<td>+325 (45µm)</td>
<td>0.1, 1, 3, 5</td>
</tr>
<tr>
<td>-325 (45µm)</td>
<td>100, 97, 95</td>
</tr>
<tr>
<td>-15µm</td>
<td>0.0, 1, 5, 10</td>
</tr>
<tr>
<td>-10µm</td>
<td>2, 5, 9</td>
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</tbody>
</table>

L-PBF Tolerance Variations for -325 (45µm) Powder

Morphology is important but usually varies little from lot to lot within a supplier
- Once a supplier is qualified, this should be a secondary concern
- Visual examination is flawed/insufficient and quantitative measures have not been standardized or correlated to AM performance
AM Procurement Considerations – Powder chemistry / cleanliness

**Powder Manufacturer**
- Metallic cross contamination
  - Powder handling practices
  - Inert handling capability
- Non-metallic contamination
  - Ceramic inclusions

**Powder User**
- Metallic Cross contamination
  - Other grades
  - System, hoppers, tubing
    - Dedicated to each grade?
    - Melt pool ejection of powder
- Non-metallic contamination
  - System
  - Airborne
- Recycling
  - Changing PSD
  - Oxidation
AM Procurement Considerations – ‘Used’ / Recycled powder

PSD Change and Oxidized Particles – CCM

- Loss of fines
- Agglomeration
- Oxidized particles

Laser Powder Bed

As Received CCM Powder
Oxygen = 260 ppm

Recycled 10x CCM Powder
Oxygen = 384 ppm

Recycled 30x CCM Powder
Oxygen = 568 ppm
Other Practical Advice / Pitfalls to Avoid

Advice
• Build with what you know – In some circumstances a known sub-optimal alloy/parameter set/mechanical property is better when time is short.
• Ask when you don’t know – Machine OEMs and material providers can help guide when considering new opportunities.
• Clean, Isolate, Inspect – Think of cross-contamination as an adversary that aims to infiltrate your defenses. Look for all weaknesses and act accordingly.
• Ignorance is not bliss – Just because you can’t see powder, doesn’t mean it’s clean.

Pitfalls to Avoid
• Basing a spec on first lot received – “well I know that worked, so to be safe I’ll just order it that way every time” = $$$ and headaches
• Falling into marketing traps – “that powder looks nice in that brochure, it must make stronger parts since it was selectively photographed to not show any non-spherical or satellited particles”
• Over-engineering specifications – Specifying values for secondary parameters when correlation between values and fit for use are not established or well known = $$$ and headaches
• Thinking more data is more accurate – More decimal points with poor sampling statistics (like with laser PSD measurements) can be misleading, especially at the tails of the distribution.
• Not re-inventing the wheel – Don’t assume conventional (cast/wrought) compositions, heat-treatments, etc. are sufficient/optimal.
Summary

- Most AM powder is produced by gas or plasma wire atomization
  - Both give acceptable quality when properly tailored for the AM application
- Sieve analysis for ≥45 µm, laser diffraction for <45 µm.
  - Tolerances for top and bottom; d50 determined by atomization process and is redundant/overconstraining.
- Flowability / spreadability is important but elusive
  - Existing methods are insufficient and work is ongoing.
- Machine throughput/needed resolution and properties drives tailored PSD and chemistry and powder cost.
- Consider differences in wrought process and AM process and determine if chemistry / heat treatment make sense and if mechanical properties are realistic.
- Remember PSD tolerances (big difference in 10-45 µm if it’s 1% or 10% max allowed -10 µm)
- Cleanliness is important
- Plan for some handling/inspection if recycling powder

- Think critically of technical marketing, avoid calibrated eyeball tests, and other advice / pitfalls to avoid from previous slide