Synthesis of particle strengthened CoCrFeNi-based HEA-CCA via laser-powder bed fusion process

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Outline

1. Introduction
2. Parameter developments of L-PBF process
3. Alloy developments
4. Nitride formation
5. Summary
1. Introduction

- **PaCCman project**
  - Title: Particle-strengthened Compositionally Complex Alloys (PaCCman)
    - Interlinking powder synthesis, additive manufacturing, microstructure evolution and deformation mechanisms
  - Objectives:
    (a) Synthesis of p-CCA via gas-atomization and L-PBF process
    (b) Investigation of the influence of L-PBF process on micro- and nanostructure
    (c) Study of deformation mechanisms of p-CCA synthesized by L-PBF process
  - Team:
    - Powder Technology: V. Uhlenwinkel, E. Gärtner
    - Additive Manufacturing: E. Jägle, H.Y. Jung
    - Deformation Mechanism: G. Dehm, N. Peter
1. Introduction

- Laser-powder bed fusion process
  (1) Near net-shape manufacturing
  (2) Rapid solidification
    → Reduction of segregation, extension of solid solubility, fine microstructure

- Research interests
  Bulk synthesis of particle strengthened CoCrFeNi-based CCA via L-PBF process
  (a) Nitrides in HEA/CCA matrix
  (b) B2 in A1 matrix, or (c) B2 in A2 matrix

CoCrFeNi  AlCoCrFeNi  AlCoCrFeMnNi

A1  B2 matrix (?)  A2 (?)

a) Effect of L-PBF process on microstructure and phase selection of HEA/CCAs
b) Precipitation behavior and its effects on strengthening mechanisms of HEA/CCAs
Outline

1. Introduction
2. Parameter developments of L-PBF process
3. Alloy developments
4. Nitride formation
5. Summary and future plans
- Powder processability (CoCrFeNi alloy)

  ▪ Chemical composition (ICP-OES)  
  
<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder</td>
<td>24.76</td>
<td>25.14</td>
<td>25.33</td>
<td>24.77</td>
</tr>
</tbody>
</table>

  ▪ Selection of particle size for L-PBF process

<table>
<thead>
<tr>
<th>Powder</th>
<th>Image</th>
<th>Flowability</th>
<th>Spreadability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CI$^1$ [%]</td>
<td>$H^2$</td>
</tr>
<tr>
<td>0-90 μm</td>
<td></td>
<td>17.2</td>
<td>1.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fair level</td>
<td></td>
</tr>
<tr>
<td>20-90 μm</td>
<td></td>
<td>14.5</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Good level</td>
<td>✓</td>
</tr>
</tbody>
</table>

  1) Compressibility index, CI
  
  \[
  CI = \left( \frac{\rho_{tap} - \rho_{bulk}}{\rho_{tap}} \right) \times 100
  \]

  2) Hausner ratio, $H$
  
  \[
  H = \frac{\rho_{tap}}{\rho_{bulk}}
  \]

Flowability and spreadability of HEA powder were improved by removal of fine particles. Powders with 20-90 μm was chosen for further parameter optimization.
- **Parameter optimization of L-PBF process**
  - Raw materials: As-atomized powder of CoCrFeNi alloy (powder size: 20-90 μm)
  - Part: Cube box (dimension: 8x8x8 mm³)
  - Hatching: Simple scanning pattern with 90° rotation

<table>
<thead>
<tr>
<th>P [W]</th>
<th>Various</th>
</tr>
</thead>
<tbody>
<tr>
<td>v [m/s]</td>
<td>Various</td>
</tr>
<tr>
<td>L [µm]</td>
<td>70</td>
</tr>
<tr>
<td>H [µm]</td>
<td>90</td>
</tr>
<tr>
<td>D [µm]</td>
<td>90</td>
</tr>
</tbody>
</table>

Scan rate [m/s] | Laser power [W] | Result
---|---|---
0.25 | 100 | 88.1 %
     | 200 | 98.6 %
     | 300 | ✓99.8 %
     | 400 |
0.50 | | 90.8 %
     | 100 | 97.1 %
     | 200 | 98.8 %
0.75 | | 93.2 %
     | 100 | 98.1 %
     | 200 | 97.9 %
1.00 | | 69.9 %
     | 100 | 89.8 %
     | 200 | 94.5 %
1.50 | |

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2. Parameters optimization of L-PBF process

- Parameter optimization of L-PBF process
  • As-built CoCrFeNi alloy fabricated by laser power of 300 W

<table>
<thead>
<tr>
<th>P [W]</th>
<th>300 W</th>
</tr>
</thead>
<tbody>
<tr>
<td>v [m/s]</td>
<td>Various</td>
</tr>
<tr>
<td>L [µm]</td>
<td>70</td>
</tr>
<tr>
<td>H [µm]</td>
<td>90</td>
</tr>
<tr>
<td>D [µm]</td>
<td>90</td>
</tr>
</tbody>
</table>

Scan rate [m/s]

Middle part

Surface

Top part

Sufficient melting and stabilized melt flow
**- Microstructure evaluation of base alloy**

- Phase analysis of CoCrFeNi alloy ($P = 300$ W, $v = 0.25$ m/s)

As-built CoCrFeNi alloy consists of single solid solution with A1 structure. The alloy has a strong crystallographic texture with a preferential $<100>$ growth along the building direction.
- Microstructure evaluation of base alloys

- Elemental distribution of CoCrFeNi alloy (P = 300 W, v = 0.25 m/s)
  - SEM_EDS analysis
  - APT analysis

The CoCrFeNi alloy has homogeneous atomic distribution in as-built condition
- Microstructure evaluation of base alloys

The AlCoCrFeNi(Mn) alloys consist of A2/B2 phase in XRD resolution
As-built AlCoCrFeMnNi alloy has strong crystallographic texture, but no elemental segregation at grain boundaries.
- Microstructure evaluation of base alloys

✓ Inhomogeneity of Mn in L-PBF samples

- Laser energy density (E) affects the temperature distribution of melt pool. The volume based energy density \( E \) (J/mm\(^3\)) is defined as

\[
E = \frac{P}{v \times h \times t}
\]

\( E = \) Energy density (J/mm\(^3\)), \( P = \) laser power (W), \( v = \) scan speed (mm/s), \( h = \) hatch spacing (mm), \( t = \) layer thickness (mm)

<table>
<thead>
<tr>
<th>Elements</th>
<th>Low input-SLM</th>
<th>High input-SLM</th>
<th>Powder</th>
<th>Ingot</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>10</td>
<td>15</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>Cr</td>
<td>15</td>
<td>20</td>
<td>25</td>
<td>20</td>
</tr>
<tr>
<td>Mn</td>
<td>20</td>
<td>25</td>
<td>30</td>
<td>25</td>
</tr>
<tr>
<td>Co</td>
<td>25</td>
<td>30</td>
<td>35</td>
<td>30</td>
</tr>
<tr>
<td>Ni</td>
<td>30</td>
<td>35</td>
<td>40</td>
<td>35</td>
</tr>
<tr>
<td>Fe</td>
<td>35</td>
<td>40</td>
<td>45</td>
<td>40</td>
</tr>
</tbody>
</table>

Owing to the low boiling temperature of Mn element, the L-PBF process involved Mn evaporation, which leads macro-scale elemental inhomogeneity of the alloys.
- Nanostructure of AlCrFeCoMnNi alloy

(a) STEM-HADDF

(b) APT reconstruction

The AlCoCrFeMnNi HEA has nano-scaled phase separation by spinodal decomposition
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5. Summary
3. Alloy developments

- **Alloys of interest**

  - **Alloying method**

    - **Powder1**
    - **Powder2**
    - Blending
    - Mixed powder
    - L-PBF
    - Bulk HEA
### 3. Alloy developments

- **Alloys of interest**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>C16.6</td>
<td>Al$<em>{16.6}$Co$</em>{16.6}$Cr$<em>{16.6}$Fe$</em>{16.6}$Mn$<em>{16.6}$Ni$</em>{16.6}$</td>
<td>A2/B2</td>
</tr>
<tr>
<td>C14.7</td>
<td>Al$<em>{14.7}$Co$</em>{17.7}$Cr$<em>{17.7}$Fe$</em>{17.7}$Mn$<em>{14.7}$Ni$</em>{17.7}$</td>
<td>A1+A2/B2</td>
</tr>
<tr>
<td>C12.5</td>
<td>Al$<em>{12.5}$Co$</em>{18.8}$Cr$<em>{18.8}$Fe$</em>{18.8}$Mn$<em>{12.5}$Ni$</em>{18.8}$</td>
<td>A1+A2/B2</td>
</tr>
<tr>
<td>C10</td>
<td>Al$<em>{10}$Co$</em>{20}$Cr$<em>{20}$Fe$</em>{20}$Mn$<em>{10}$Ni$</em>{20}$</td>
<td>A1</td>
</tr>
<tr>
<td>C0</td>
<td>Co$<em>{25}$Cr$</em>{25}$Fe$<em>{25}$Ni$</em>{25}$</td>
<td>A1</td>
</tr>
</tbody>
</table>

The powder blending method was effective to design alloys forming desired phases by L-PBF process. The composition range of A1 phase was extended.

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3. Alloy developments

- Phase selection of HEA processed by L-PBF

✓ Conventional parameters for phase prediction in HEA
  S. Guo et al. / Prog. Nat. Sci. 21 (2011) 433-446.

a) Valence electron concentration (VEC)

b) $\Delta H_{\text{mix}}$ (enthalpy of mixing) and $\delta$ (atomic radius difference)

c) CALPHAD, MD or Ab initio computational approaches

Phase prediction ≠ Experimental results (from L-PBF process)

✓ Reason for the expansion of A1 phase range

a) Al addition (leading lattice distortion and stabilization of BCC structure)

b) Rapid solidification rate (about $10^4$~$10^6$ K/s) → solubility limits↑

For the alloy development for or by L-PBF process, the rapid solidification effect should be considered.
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- Nitride formation during L-PBF process

- Role of gas flow in L-PBF process
  - Removal of process by-products (spatter and welding fumes), protection of oxide formation (in case of inert gas)

- Type of gas generally used in L-PBF process

<table>
<thead>
<tr>
<th></th>
<th>Ar</th>
<th>N₂</th>
<th>He</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass</td>
<td>40</td>
<td>28</td>
<td>4</td>
</tr>
<tr>
<td>The first ionization potential [eV]</td>
<td>15.68</td>
<td>14.54</td>
<td>24.46</td>
</tr>
<tr>
<td>Relative density of gas (air = 1)</td>
<td>1.38</td>
<td>0.97</td>
<td>0.14</td>
</tr>
<tr>
<td>Thermal conductivity [W/mK]</td>
<td>0.018</td>
<td>0.026</td>
<td>0.151</td>
</tr>
</tbody>
</table>

- Gas atmosphere effects plasma, penetration depth and melting behavior of the materials

Gas is important factor for L-PBF process and materials properties
4. Nitride formation

- Nitride formation during L-PBF process

AlCoCrFeNiMn alloy (laser powder = 200 W, scan rate = 0.50 m/s)

Using reactive N₂ gas flow during L-PBF process lead a formation of AlN particles.
4. Nitride formation

- Nitride formation during L-PBF process

AlCoCrFeNiMn alloy (laser powder = 200 W, scan rate = 0.50 m/s)

L-PBF process under N₂ gas flow formed cubic AlN in A2/B2 matrix. The formation of cubic-nitride indicates the strong influence of rapid solidification rate of L-PBF process.
Summary

1. We investigated the influence of L-PBF process on micro- and nanostructure of CoCrFeNi and the Al-containing CoCrFeNi(Mn) alloy
   - Phase formation: CoCrFeNi alloy - A1 phase,
     Al-containing CoCrFeNi(Mn) alloy - A2/B2 phase
   - Nano-scaled modulated structure formed by spinodal decomposition

2. Alloy development method using powder blending and L-PBF process was effective to design HEAs consisted of desired phases

3. Nano-scaled nitrides were homogenously formed in AlCoCrFeNi(Mn) alloy by N₂ gas flow
Thank you for your attention!

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