Manifattura Additiva di Ceramici
Caratteristiche e Prospettive

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**Europe Makes Ceramics** is an initiative of the European Ceramic Society, under the umbrella of its R&D working group, which aims at building a network of young scientists and professionals working in the field of AM of ceramic materials.

The **young Ceramists Additive Manufacturing Forum** (yCAM) is an event and networking platform organized by EMC and supported by the JECS Trust, dedicated to all young researchers interested in the AM of ceramics.

→ 3-4/5/2018, Padova
Additive Manufacturing (AM)

Process of joining materials to make *parts* from 3D model data, usually *layer upon layer*, as opposed to subtractive manufacturing and formative manufacturing methodologies.

Note: Historical terms: rapid prototyping, 3D printing, additive fabrication, additive processes, additive techniques, additive layer manufacturing, layer manufacturing, solid freeform fabrication and freeform fabrication.
AM of Ceramics: general comments

• AM is not substituting subtractive and formative technologies; rather, it complements them (for example for complex geometries, small batches, flexible production, spare parts, prototypes, customized products, materials which are difficult to shape, …)

• Therefore, before selecting an AM technology for a certain component, it makes sense to evaluate if AM is advantageous over traditional technologies (use it where it really is the best solution not because it is possible to use it!)

• AM of ceramics is more difficult than AM of polymers and metals, and therefore it has both a less developed state of the art and industrial applications.

• A few ceramic systems have been widely used (also as commercial product), since the beginning of AM, like gypsum and sand.

• Developments in the past few years allowed for the first examples and industrialization of AM of technical ceramics
AM of ceramics: main features

Many of the processing issues involved in AM of ceramics are the same as those that characterize ceramic processing in general:

- packing density
- sintering
- composition

The most difficult part in AM of ceramics is not the AM process itself, but what comes afterwards:

- debinding
- sintering / infiltration

Existing AM technologies are intrinsically particularly suited for the generation of porous ceramics.

- Complex-shaped porous architectures with a precise control of the dimension, shape and amount of pores: new fields of research and applications
AM of ceramics: challenges

Very few AM technologies are capable of generating fully dense monolithic ceramic bodies:

- conventional advanced ceramics production requires very fine powders
- poor flowability and low packing density

Ceramic suspensions or pastes: significant amount of organics →

- limitations in wall thickness and part volume: very slow heating process to avoid surface defects

Sintering defines the microstructure, the phase composition and physical-chemical properties of the component.
Additive Manufacturing of ceramics

- **Indirect AM**: first a layer of material is deposited, then the cross section (slice) of the part is inscribed in the layer and then the excess material surrounding the part is removed to release the final object → Powder-bed (3DP), Selective Laser Sintering (SLS), Stereolithography (SLA), Digital Light Processing (DLP), Laminated Object Manufacturing (LOM)

- **Direct AM**: the material is directly deposited only in the position giving the desired shape of the final object → Direct Ink Writing/Robocasting (DIW), Inkject printing (IP), Fused Deposition Modeling (FDM)

• **Basic working principle**: selective curing (cross-linking) of a polymeric resin by means of an energy source (UV or visible light)
• A typical SLA/DLP mixture contains:

1) Monomers or oligomers; 2) Photoinitiator; 3) Diluent (usually reactive); 4) Additives; 5) Catalyst; 6) Absorber; 7) Ceramic powders

• Resin suspensions filled with ceramic particles can be used to produce high quality ceramic components via the following route:

1) SL of a highly filled suspension (> 40 vol%) to produce a “green part”

2) Debinding of the “green part” to burn the organics and produce a “brown part”. **Critical step**, for the risk of creating defects due to the high gas release

3) High temperature firing of the “brown part” to produce the final sintered ceramic part
- Alumina
- Grain size ca. 3 μm
- 4 points bending strength 427 MPa (99.3% of theoretical density)
- **Basic working principle**: a liquid bonding agent is selectively deposited to join powder materials.
- Flowability of the powder is very important (fine powders (< 20 μm) tend to flow poorly, especially ceramics!)
Choice of Binder

There are several possible combinations of printing liquids, or “binders”. For ceramics there are 3 possibilities:

1) The printing liquid is a solvent in which a polymeric “glue” is dissolved

2) The printing liquid is a solvent and a polymeric binder is mixed within the ceramic powder

3) The printing liquid (typically inorganic - or water - in this case) induces a “setting” reaction in the ceramic material
Sand casting cores

Bioceramics

Schunk IntrinSiC (Si infiltration)
Inkjet Printing (IP)

- **Basic working principle**: droplets of the building material are selectively deposited.
- The theory of inkjet printing of liquid drops was developed originally for the printing of inks for paper printing.
- It models the properties of the ink needed to have the formation of stable drops.
- Ceramic inks have higher density than inks formulated for paper printing and therefore different inertial behavior.
R. Noguera et al., “3D fine scale ceramic components formed by ink-jet prototyping process,” Journal of the European Ceramic Society, (2005) 25, 2055-2059


Some limitations on shapes and aspect ratios exist with this technology.
Powder Bed Fusion (SLS)

- **Basic working principle**: selective sintering/melting of a powder bed by means of an energy source: 1) Laser → Selective laser sintering/melting (SLS/SLM); 2) Electron beam → Electron beam melting (EBM)
- Very difficult to obtain defect-free ceramic parts by SLS/SLM
Issues

• High sintering and melting temperatures
• Poor resistance to thermal shock
• Preheating to reduce thermal shock is possible
• Short interaction time between laser and powder limits material diffusion, leading to poor sintering and residual porosity
• Formation of micro cracks

![Image of laser interaction and microcracks](image_url)
**Basic working principle:** 1) selective deposition of a paste extruded through a nozzle (also commonly named Robocasting); 2) melting of a filament containing ceramic particles

- DIW relies on the rheological properties of the paste in order to maintain the shape of the deposited material, while FDM relies on the fast cooling of the polymer melt
Challenge: thin walls and spanning features
→ optimization of the ink rheology

Requirements
• Initial yield stress
• Low viscosity during extrusion
• High viscosity after extrusion

• → yield pseudoplastic behavior
• → strong physical (reversible) gel
Rheological design of the ink

The pseudoplastic (with yield stress) behavior of the ink can be achieved following different approaches:

1. Through evaporation of a solvent. This is the easiest way, but it is limited to large nozzle diameters, otherwise clogging of the nozzle occurs.
2. Flocculation/coagulation of the suspension.
3. Use of reversible (physical) gels.
4. Use of thermo-reversible gels.

Fumed silica forms a reversible gel with pseudoplastic rheology.
Incorrect ink design → sagging

Correct ink design → spanning features
Laminated Object Manufacturing (LOM)

- **Basic working principle**: sheets of a material are selectively cut and bonded to form an object
- No binder needed
- Moderate strength
- Defects at the intersection between sheets: delamination, porosity, differential shrinkage
LOM of preceramic tapes

a) SiSiC,
b) Al$_2$O$_3$,
c) LZSA glass-ceramic
d) Si–SiC–SiOC–N microcomposite

Indirect AM technologies

- Higher speed
- Simpler rheology requirements
- Higher design flexibility but some limitations for materials
- Filler can adsorb heat

- Poorer adhesion between layers
- Higher residual porosity
- Lower spatial flexibility
- Complex powder mixture required to ensure flowability
Direct AM technologies

- Better adhesion between layers
- Higher packing densities
- Higher green densities
- Larger printing envelopes

- Limited by short reaction times
- Limited complexity without support material
- Heat development can cause issues
# Comparison between AM technologies

<table>
<thead>
<tr>
<th>Technology</th>
<th>Plus</th>
<th>Minus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vat photopolimerization</td>
<td>• Very good resolution (down to 20 μm)</td>
<td>• Debinding is difficult and long for thick parts</td>
</tr>
<tr>
<td></td>
<td>• Dense and fine microstructure also for technical ceramics</td>
<td>• Restricted to wall thickness &lt; 10-20 mm</td>
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<tr>
<td></td>
<td></td>
<td>• Needs support structures</td>
</tr>
<tr>
<td>Material Extrusion</td>
<td>• Very flexible as material’s choice</td>
<td>• Limited geometrical flexibility</td>
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<tr>
<td></td>
<td>• Can produce from small to very large parts</td>
<td>• Surface quality depends on the stacking of the filaments</td>
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<tr>
<td></td>
<td>• Potentially fast, depending on the geometry and diameter of the nozzle (0.1 mm to cm)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Dense and fine microstructure also for technical ceramics</td>
<td></td>
</tr>
<tr>
<td>Material Jetting</td>
<td>• Dense and fine microstructure also for technical ceramics</td>
<td>• Potential problems with clogging of the printing head</td>
</tr>
<tr>
<td></td>
<td>• Potential for multimaterial parts</td>
<td>• Slow for large parts</td>
</tr>
<tr>
<td></td>
<td>• Good resolution (&lt; 100 μm)</td>
<td>• Needs support material</td>
</tr>
<tr>
<td>Binder Jetting</td>
<td>• Fast for medium-large areas</td>
<td>• Medium resolution (100-200 μm)</td>
</tr>
<tr>
<td></td>
<td>• Flexible, easy to use with new materials</td>
<td>• Cannot produce a dense and fine microstructure for technical ceramics</td>
</tr>
<tr>
<td></td>
<td>• Usually no need of support structures</td>
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</tbody>
</table>
Summary

- **Liquid or paste-based technologies** (SLA/DLP, IP, DIW, FDM, LOM) can use finer ceramic particles and can achieve high packing densities → it is possible to sinter also technical ceramics to high density.

- **Powder-based technologies** (3DP, SLS) can only use coarser particles and achieve lower packing density, restricting the sinterability of the green parts → residual porosity (unless post-infiltration is used).
### Selection of AM processes for ceramics

**Dimensions**
- Small (< 50-100 mm)
- Medium (0.1-1 m)
- Large (1-10 m)

**Wall thickness**
- Thin walls/struts (< 10-20 mm)
- Thick walls (> 10 mm)

**Porosity after sintering***
- > 99% dense microstructure
- > 80% dense microstructure
- Porous microstructure (20-50%)

**Starting ceramic powder used**
- Fine (< 20 μm, often < 1 μm)
- Coarse (20 – 200 μm)

**Surface roughness/quality**
- Very smooth (few μm)
- Smooth (tenths of μm)
- Rough (hundreds of μm)

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*It depends also on the specific material. Also, some ceramics (e.g. SiSiC) are infiltrated*

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<table>
<thead>
<tr>
<th>Dimensions</th>
<th>Vat Photo</th>
<th>Mat ext</th>
<th>Mat Jett</th>
<th>Powder 3DP</th>
<th>SLS</th>
<th>LSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Medium</td>
<td>✔</td>
<td>✔</td>
<td>✓</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Large</td>
<td>✔</td>
<td>✔</td>
<td>X</td>
<td>X</td>
<td>✔</td>
<td>X</td>
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<thead>
<tr>
<th>Wall thickn.</th>
<th>Vat Photo</th>
<th>Mat ext</th>
<th>Mat Jett</th>
<th>Powder 3DP</th>
<th>SLS</th>
<th>LSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Thick</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
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</table>

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<thead>
<tr>
<th>Microstr.</th>
<th>Vat Photo</th>
<th>Mat ext</th>
<th>Mat Jett</th>
<th>Powder 3DP</th>
<th>SLS</th>
<th>LSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dense</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>X</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Porous</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Powder used</th>
<th>Vat Photo</th>
<th>Mat ext</th>
<th>Mat Jett</th>
<th>Powder 3DP</th>
<th>SLS</th>
<th>LSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>X</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Coarse</td>
<td>✔</td>
<td>✔</td>
<td>X</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Surface qual.</th>
<th>Vat Photo</th>
<th>Mat ext</th>
<th>Mat Jett</th>
<th>Powder 3DP</th>
<th>SLS</th>
<th>LSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very smooth</td>
<td>✔</td>
<td>X</td>
<td>✔</td>
<td>X</td>
<td>✔</td>
<td>✗</td>
</tr>
<tr>
<td>Smooth</td>
<td>✔</td>
<td>X</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Rough</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
</tr>
</tbody>
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Layerwise slurry deposition
# AM of ceramics: case studies

<table>
<thead>
<tr>
<th>Component</th>
<th>Dimensions</th>
<th>Wall thickness</th>
<th>Microstructural porosity</th>
<th>Ceramic powder</th>
<th>Surface quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina components for the textile industry</td>
<td>Small</td>
<td>Thin</td>
<td>&lt; 1%</td>
<td>&lt; 1 μm</td>
<td>Very smooth</td>
</tr>
<tr>
<td>Bioceramic implant for biomedical applications (e.g. HA, TCP)</td>
<td>Small</td>
<td>Thin</td>
<td>20-50%</td>
<td>&lt; 100 μm</td>
<td>Rough</td>
</tr>
<tr>
<td>Filter for metal casting (e.g. ATZ or mullite)</td>
<td>Medium</td>
<td>Thin</td>
<td>&lt; 1%</td>
<td>&lt; 1 μm</td>
<td>Smooth</td>
</tr>
<tr>
<td>Mould for metal casting (e.g. sand)</td>
<td>Medium-Large</td>
<td>Thick</td>
<td>20-50%</td>
<td>&lt; 1 mm</td>
<td>Rough</td>
</tr>
<tr>
<td>House</td>
<td>Large</td>
<td>Thick</td>
<td>10-30%</td>
<td>&lt; mm</td>
<td></td>
</tr>
<tr>
<td>Support for satellite mirrors ((\text{Si}_3\text{N}_4, \text{SiC}))</td>
<td>Large</td>
<td>Thick</td>
<td>&lt; 1%</td>
<td>&lt; 1 μm</td>
<td>Smooth</td>
</tr>
<tr>
<td>Rotor for large pump ((\text{SiC}, \text{Al}_2\text{O}_3, \text{ZrO}_2, \text{Si}_3\text{N}_4))</td>
<td>Medium</td>
<td>Thick</td>
<td>&lt; 1%</td>
<td>&lt; 1 μm</td>
<td>Smooth</td>
</tr>
<tr>
<td>Technical porcelain labware</td>
<td>Small-Medium</td>
<td>Thin-Thick</td>
<td>0% open porosity</td>
<td>&lt; 1 μm – 100 μm</td>
<td>Smooth</td>
</tr>
</tbody>
</table>
## AM of ceramics: case studies

<table>
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<th>Dimensions</th>
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<th>Surface quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina components for the textile industry</td>
<td></td>
<td>Thin</td>
<td>0-5%</td>
<td>Powder-based 3DP</td>
<td>Rough</td>
</tr>
<tr>
<td>Bioceramic implant for biomedical applications (e.g. HA, TCP)</td>
<td>Small</td>
<td>Thin</td>
<td>20-50%</td>
<td>Powder-based 3DP; Vat photopolymerization; Material extrusion; Material Jetting (order depends on part specs)</td>
<td>Rough</td>
</tr>
<tr>
<td>Filter for metal casting (e.g. ATZ or mullite)</td>
<td></td>
<td></td>
<td></td>
<td>1) Material Extrusion; 2) Vat photopolymerization;</td>
<td></td>
</tr>
<tr>
<td>Mould for metal casting (e.g. sand)</td>
<td></td>
<td></td>
<td></td>
<td>1) Powder-based 3DP</td>
<td></td>
</tr>
<tr>
<td>House</td>
<td></td>
<td></td>
<td></td>
<td>1) Material extrusion (extrusion of concrete)</td>
<td>Smooth</td>
</tr>
<tr>
<td>Support for satellite mirrors (Si₃N₄, SiC)</td>
<td></td>
<td></td>
<td></td>
<td>? New technologies needed</td>
<td></td>
</tr>
<tr>
<td>Rotor for large pump (SiC, Al₂O₃, ZrO₂, Si₃N₄)</td>
<td></td>
<td></td>
<td></td>
<td>1) LSD</td>
<td></td>
</tr>
<tr>
<td>Technical porcelain labware</td>
<td></td>
<td></td>
<td></td>
<td>LSD; Material extrusion; Vat photopolymerization (order depends on part specs)</td>
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</tbody>
</table>
Large scale (2x2x2 m³) AM of artificial stone, sand and refractory materials using inorganic binders (in collaboration with Desamanera, Rovigo). Printing speed: 2x2 m² (5 mm height) in 30 s.

Artificial coral reef

Indian Girl, The Metropolitan
Additive stone manufacturing

Printing of 1st layer

Removal of excess powder (printing of the part is finished)

Coated part
2 Photon Polymerization (2PP)

Use of Preceramic Polymers

Submicron resolution

In collaboration with G. Brusatin (UNIPD)
DIW of CMCs

Use of Preceramic Polymers + chopped fibers

Ceramic Matrix Composites

Aligned fibers
DIW of Geopolymers

Use of geopolymers (4D printing)

- Reactive mixture
- Geopolymerization proceeds with time
- Time-dependent rheology

- Complex, single wall shapes
- Proposed application: filters
AM of ceramics: conclusions

AM of ceramics:
• Is different than molding, machining, casting and forming
• Overturns the understanding of cost drivers, time impacts and possibilities
• Modifies reality for design, manufacturing processes and conventional wisdom

but
• Engineers need to rethink and learn new ways to design
• Consider entire process chain to realize its full value
• Additional benefits for customers must be higher than the cost of production

and
• Don´t underestimate its real potential and limit it to traditional applications expecting the same output
AM of ceramics: future

- Further development of technologies
- High resolution printing (finer details)
- Hybrid technologies (combination of technologies)
- Selection of most appropriate AM technology for the production of a specific component
- Large scale printing