Blue Skies, Greener Future: Additive Manufacturing of Ceramics

UCL

UNIVERSITÀ
DEGLI STUDI
DI PADOVA

PennState

Prof. ing. Paolo Colombo
Department of Industrial Engineering
University of Padova
and
Adjunct Professor, Dept. of Materials Science and Engineering, The Pennsylvania State University
and
Honorary Professor, Dept. of Mechanical Engineering,
University College London

paolo.colombo@unipd.it

CERAM
GLASS
RESEARCH · GROUP

Shaping of materials: three basic principles

Formative shaping

- Forging
- Bending
- Casting
- Injection molding
- Compaction of green bodies
- Conventional powder metallurgy
- Ceramic processing
- etc.

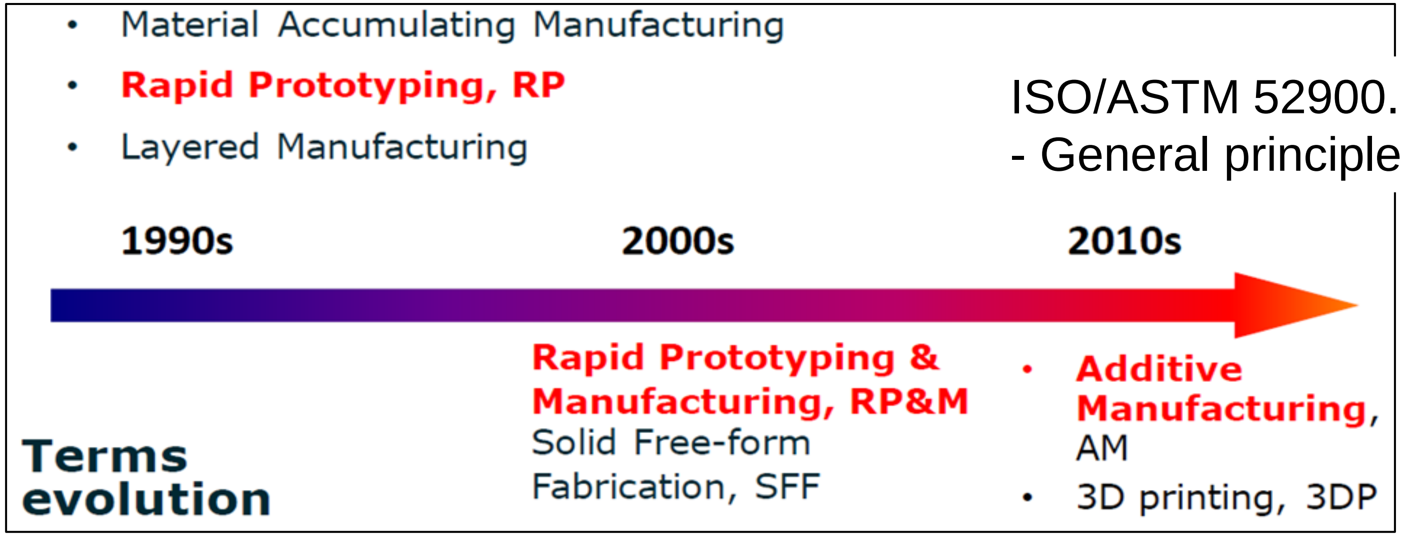
Subtractive shaping

- Milling
- Turning
- Drilling
- Electrical discharge machining
- etc.

Additive shaping

- Vat photo-polymerization
- Material jetting
- Binder jetting
- Powder bed fusion
- Material extrusion
- Directed energy deposition
- Sheet lamination
- etc. (Hybrid)

- Additive manufacturing (AM) is a technology which has the potential not only to change the way of conventional industrial manufacturing processes, adding material instead of subtracting, but also to create entirely new production and business strategies
- Currently, it is possible to manufacture ceramic components with a very wide range of compositions in a size ranging **from the sub-micron to the meter** and beyond



- Material Accumulating Manufacturing
- **Rapid Prototyping, RP**
- Layered Manufacturing

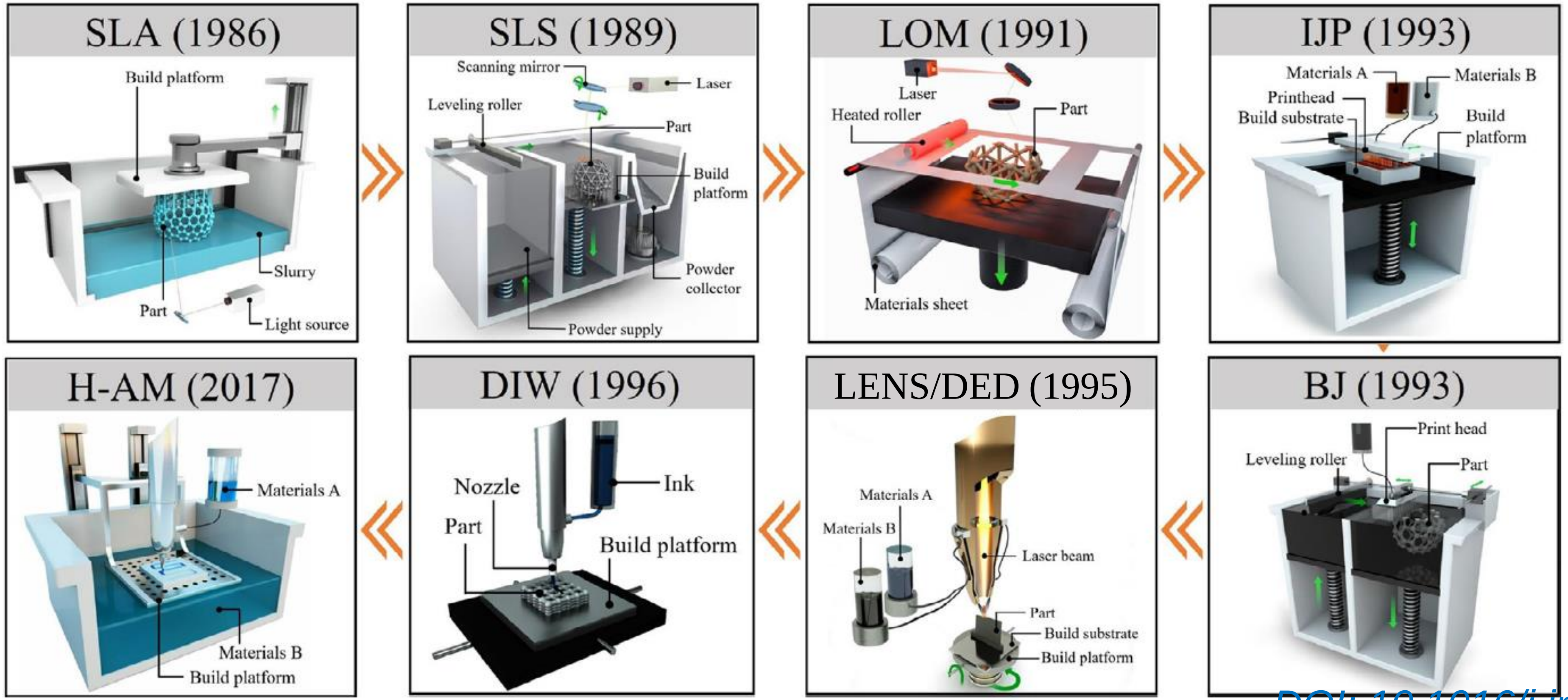
1990s **2000s** **2010s**

Rapid Prototyping & Manufacturing, RP&M
Solid Free-form Fabrication, SFF

- **Additive Manufacturing,** AM
- 3D printing, 3DP

Terms evolution

ISO/ASTM 52900. Additive manufacturing - General principles – Terminology (2022)

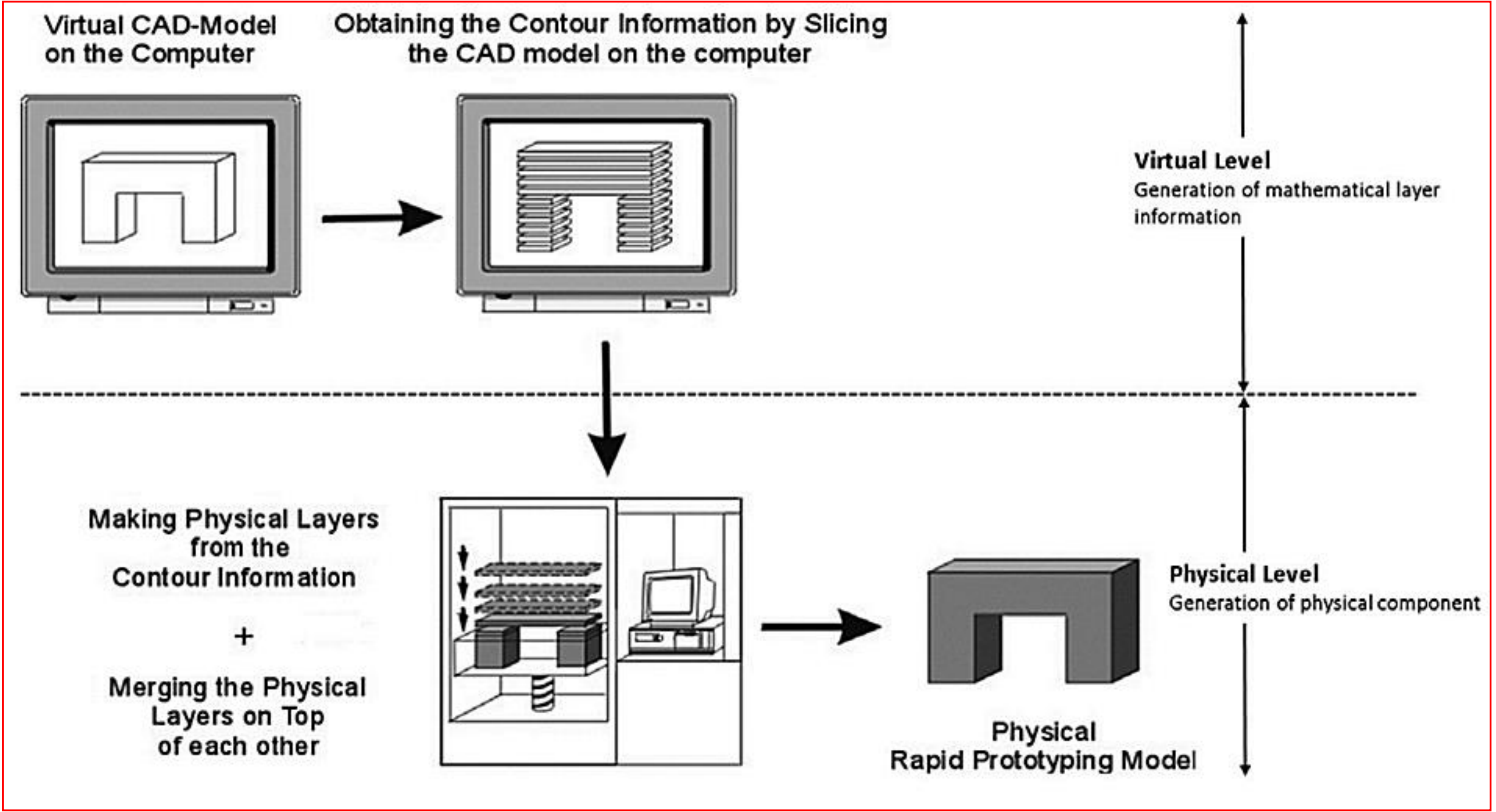


DOI: 10.1016/j.jmst.2022.06.039

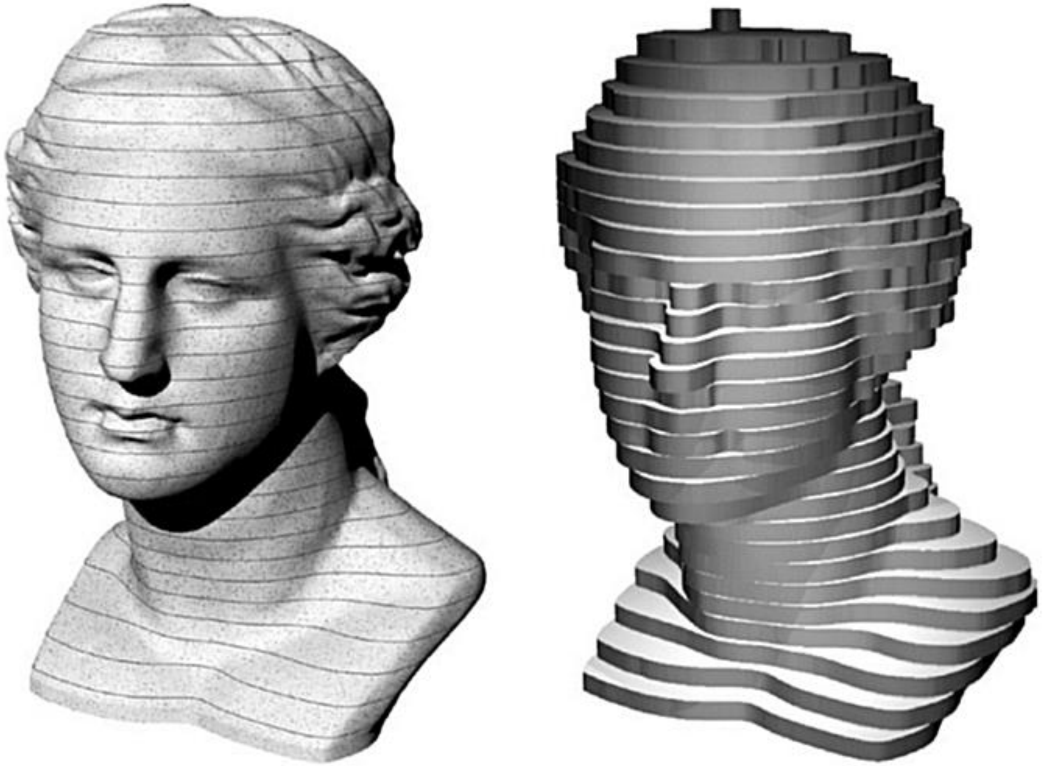
Additive Manufacturing (AM)

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, and freeform fabrication.

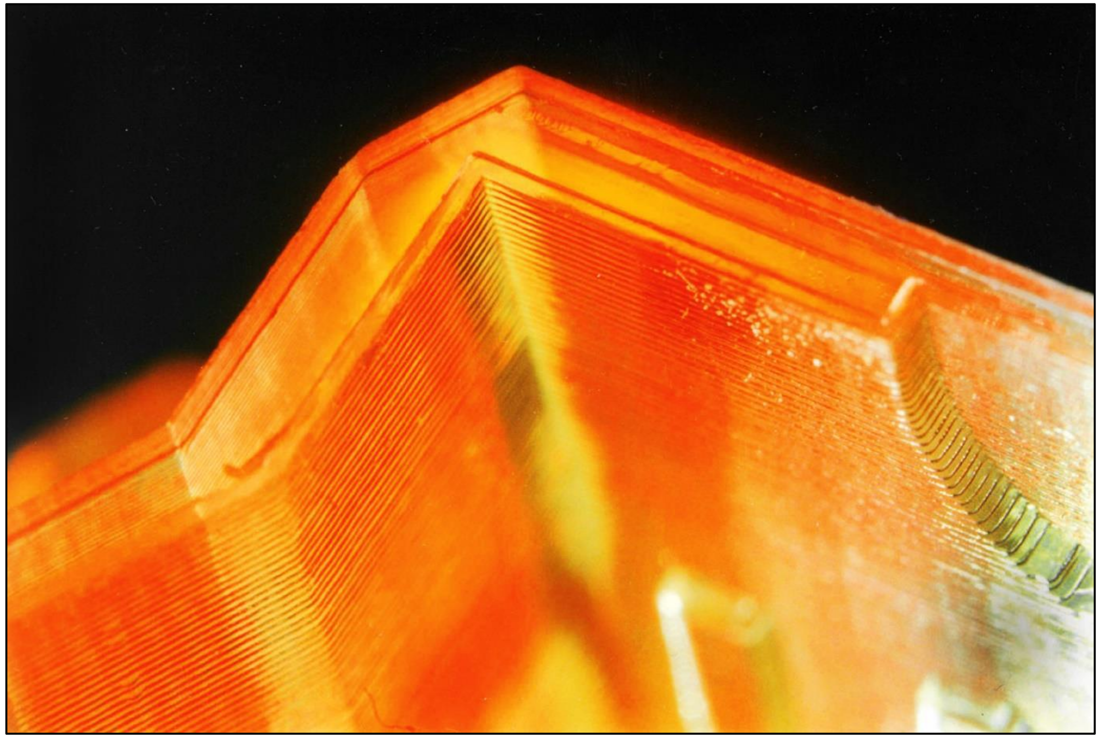


A. Gebhardt, Understanding Additive Manufacturing: Rapid Prototyping - Rapid Tooling – Rapid Manufacturing. Hanser Publications Cincinnati, OH, 2012



Stepped surface as a result of the layering process

Three-dimensional solid model (left) with marked equidistant layers and the created layer model (right)



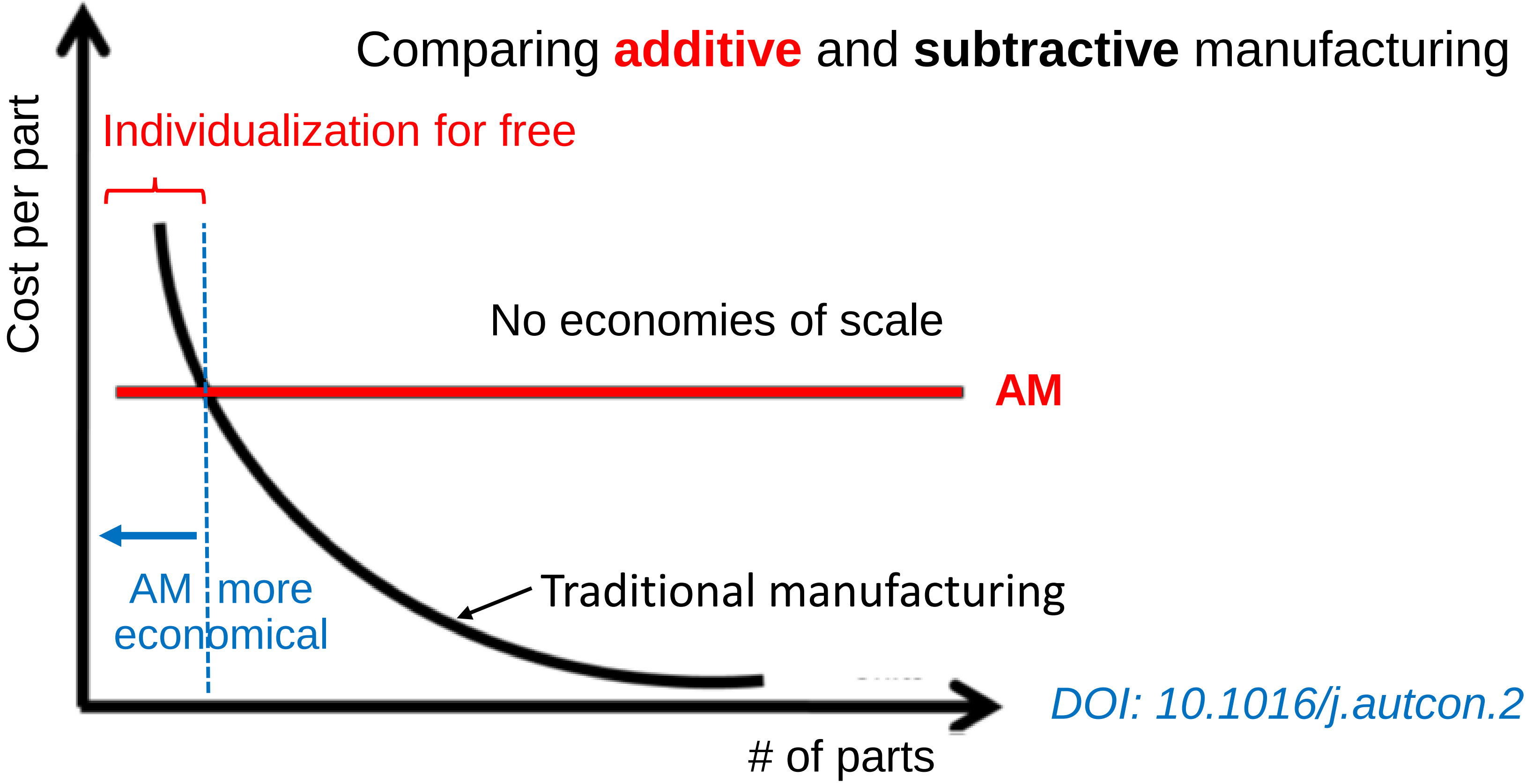
Stair-step effect in a stereolithography component
(layer thickness = 125 µm)

I. Gibson, D. Rosen, B. Stucker, Additive Manufacturing Technologies, Springer. New York, NY (2015)

Advantages of AM technologies

- No need for tools or molds
- Fast time from design to product
- Cost efficient for small series production
- Possibility of making customized products
- Possibility of producing highly complex geometries which are difficult or impossible to produce by subtractive or formative technologies.
- The cost/part is much less influenced by the geometrical complexity than in traditional technologies
- Potentially material-efficient (reduce waste) and energy-efficient
- Suitable for just-in-time production and low inventories
- Product development becomes continuous and distributed
- Time and space are no longer an issue (easier logistics and supply chain management)

The end of economies of scale?

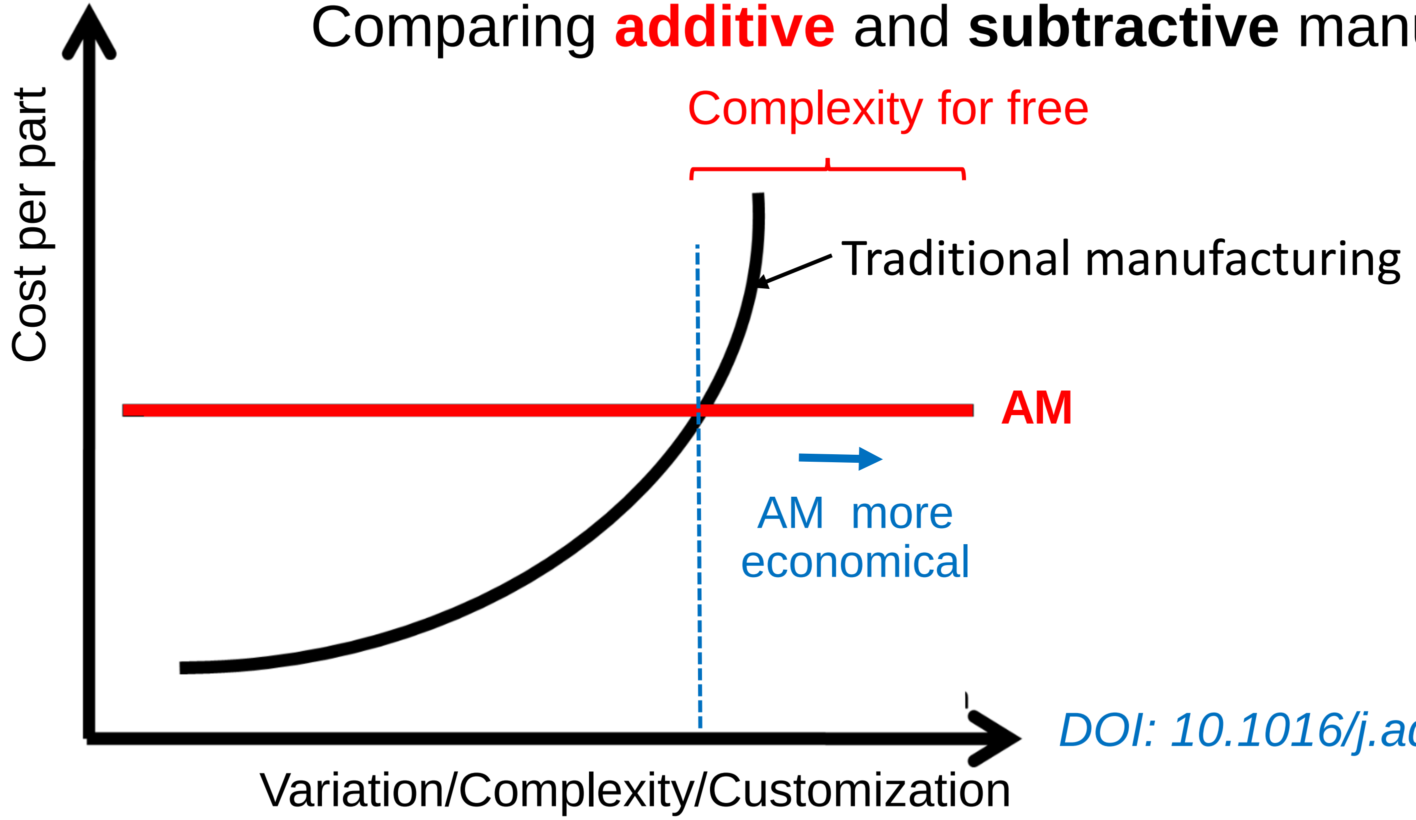

Comparing **additive** and **subtractive** manufacturing

DOI: 10.1016/j.autcon.2011.06.010

- As volumes increase in a (**subtractive**) manufacturing process, the cost for each unit of output decreases since the fixed cost can be spread across more units
- Additive manufacturing, on the other hand, implies that economies of scale become much less important. The first unit will be as expensive or cheap as the tenth or the hundredth one. In the case when you own a 3D printer, it can still be regarded as a fixed cost, but in this case it is significantly smaller

Variation and complexity are no longer expensive!

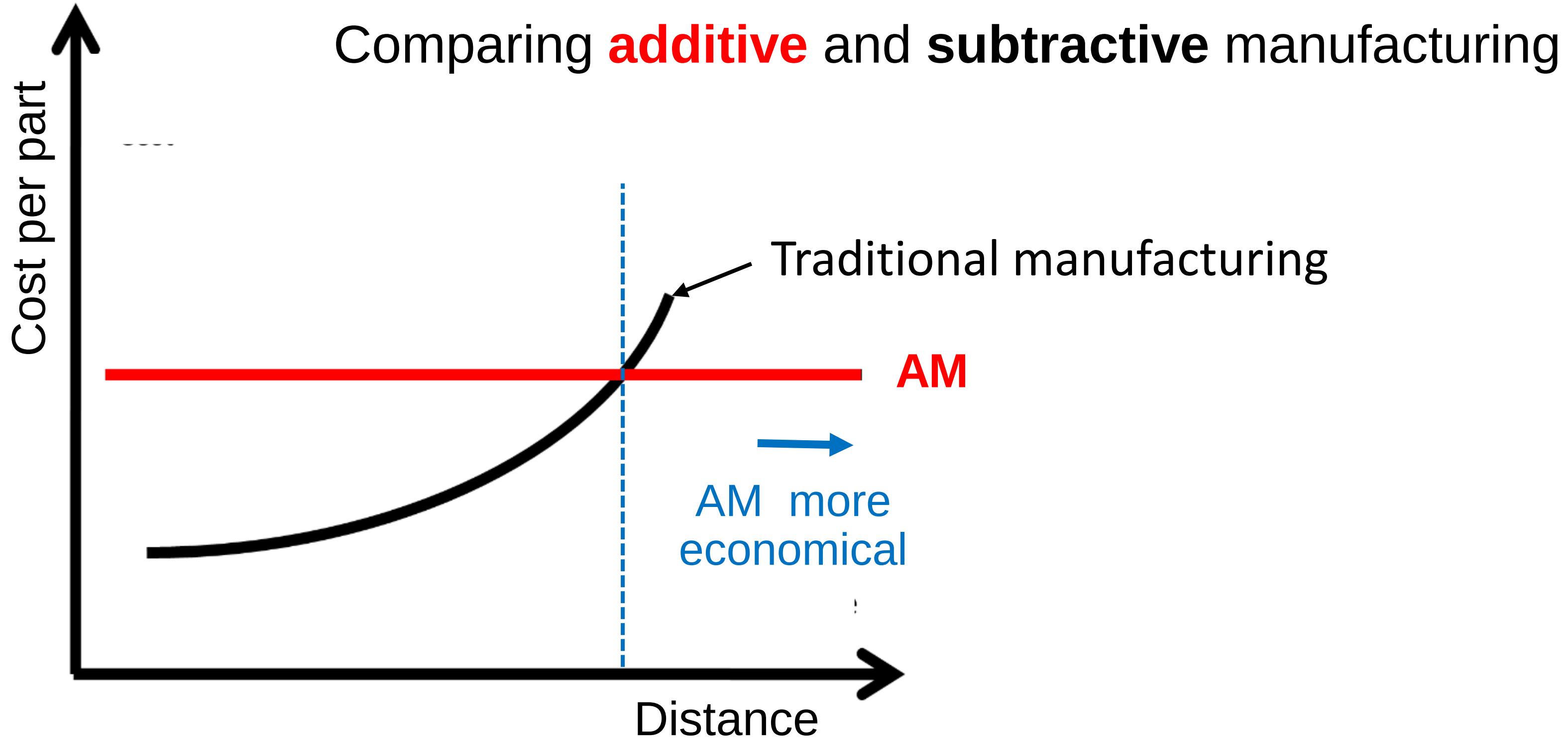
Comparing **additive** and **subtractive** manufacturing



DOI: 10.1016/j.addma.2014.08.005

- AM is unique as there is no longer a tradeoff between cost and variation! Variation/Complexity/Customization does not result in additional costs on behalf of the manufacturer
- AM is being rapidly adopted in those applications where the need for variation is very high, but has been too costly to accomplish through subtractive manufacturing techniques (e.g., dental and medical implants were early adopters of the technology as personalization can be accomplished at a low cost)

Time and space no longer an issue?

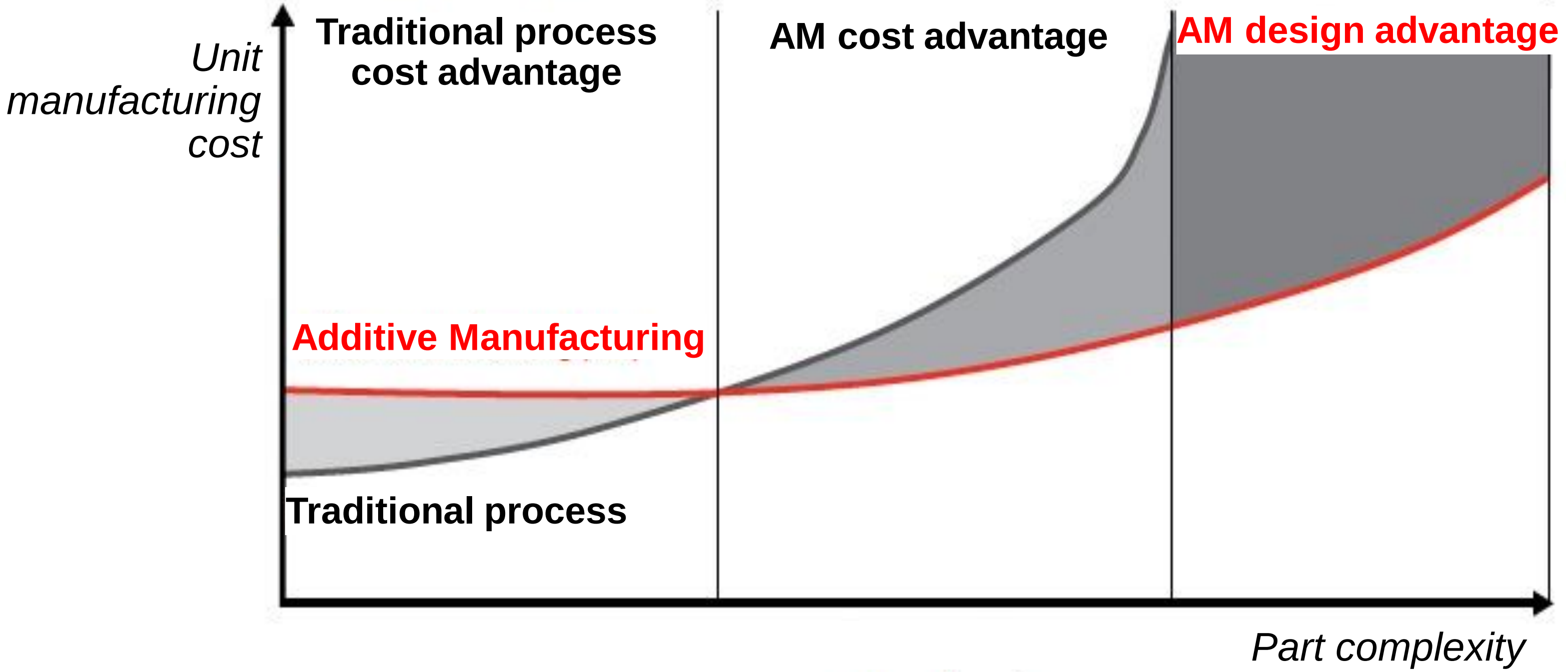


- Subtractive manufacturing requires complex logistics and supply chain management. The right inputs need to be available at the right place, at the right time. Managing inventories, lead times, process times, etc. is by no means a trivial task
- With AM, it becomes a lot easier to cope with time and space. Files can be sent electronically to one place where an object is printed when it is needed, the only required logistics would be related to the input material and the printer itself in the first place. The right thing, at the right time, without all the complexities related to transportation of components and inputs back and forth across the planet

The cost of complexity is no longer a design barrier

Additive manufacturing enables entirely new designs of components

- Lightweight
- Less material
- Improved mechanical properties
- More durable



www.bain.com

Application example

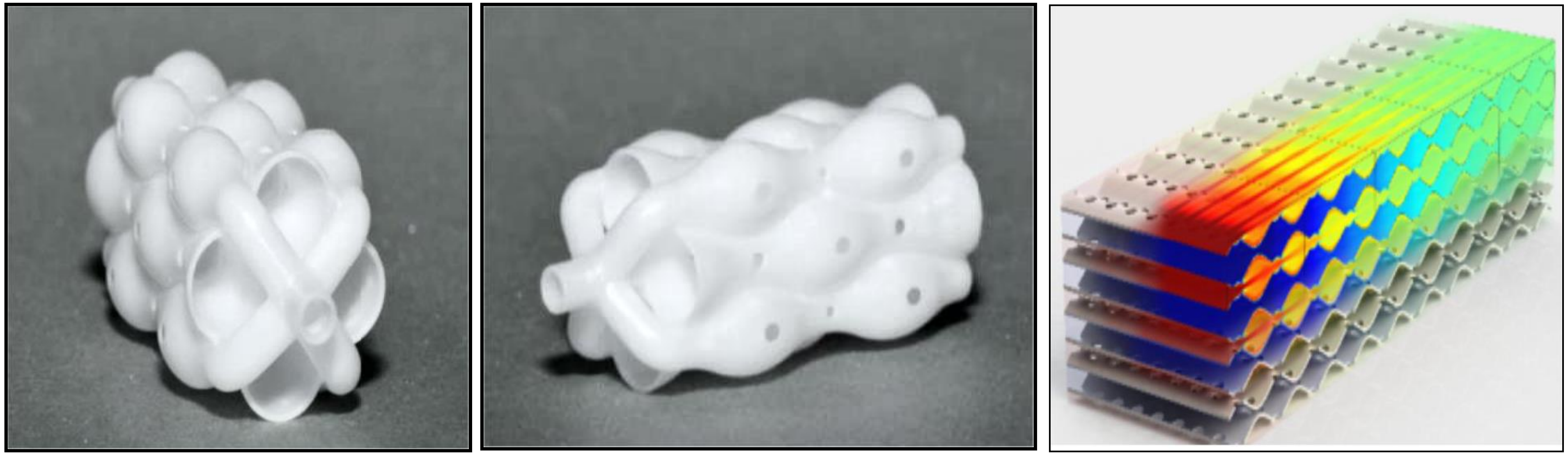
Move from a **Manufacture driven design strategy** to a **Design-for-Performance driven strategy**

New design of a catalyst carrier

- Completely new design
- Improved efficiency due to turbulent flow
- Shorter reaction way
- Less material for carrier / mixer

Fraunhofer IKTS

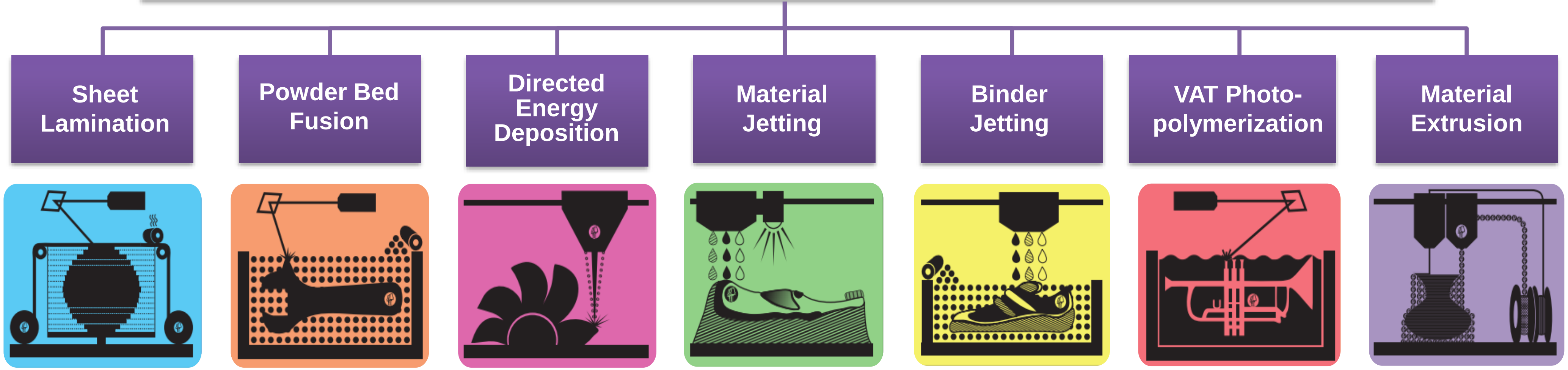
LITHOZ



Disadvantages of AM technologies

- Printers are expensive
- The technology does not provide easy means for scalable production
- Production rate per machine is limited by a range of factors – including material type
- The cost per single part is still high
- Traditional finishing is still required for many parts (also, precision issues)
- The material properties of many parts produced by AM are not comparable (worse) to traditionally produced parts.
- The properties of AM produced parts are often anisotropic.
- The is a limited choice of materials, either because of technological limits, or because new material have not been qualified yet, resulting in higher costs and lower flexibility
- Lack of AM talent, particularly with regard to the creation of objects

Additive Manufacturing technologies (ISO/ASTM 52900:2022)



- Sheet Lamination
- Powder Bed Fusion
- Directed Energy Deposition
- Material Jetting
- Binder Jetting
- VAT Photo-polymerization
- Material Extrusion

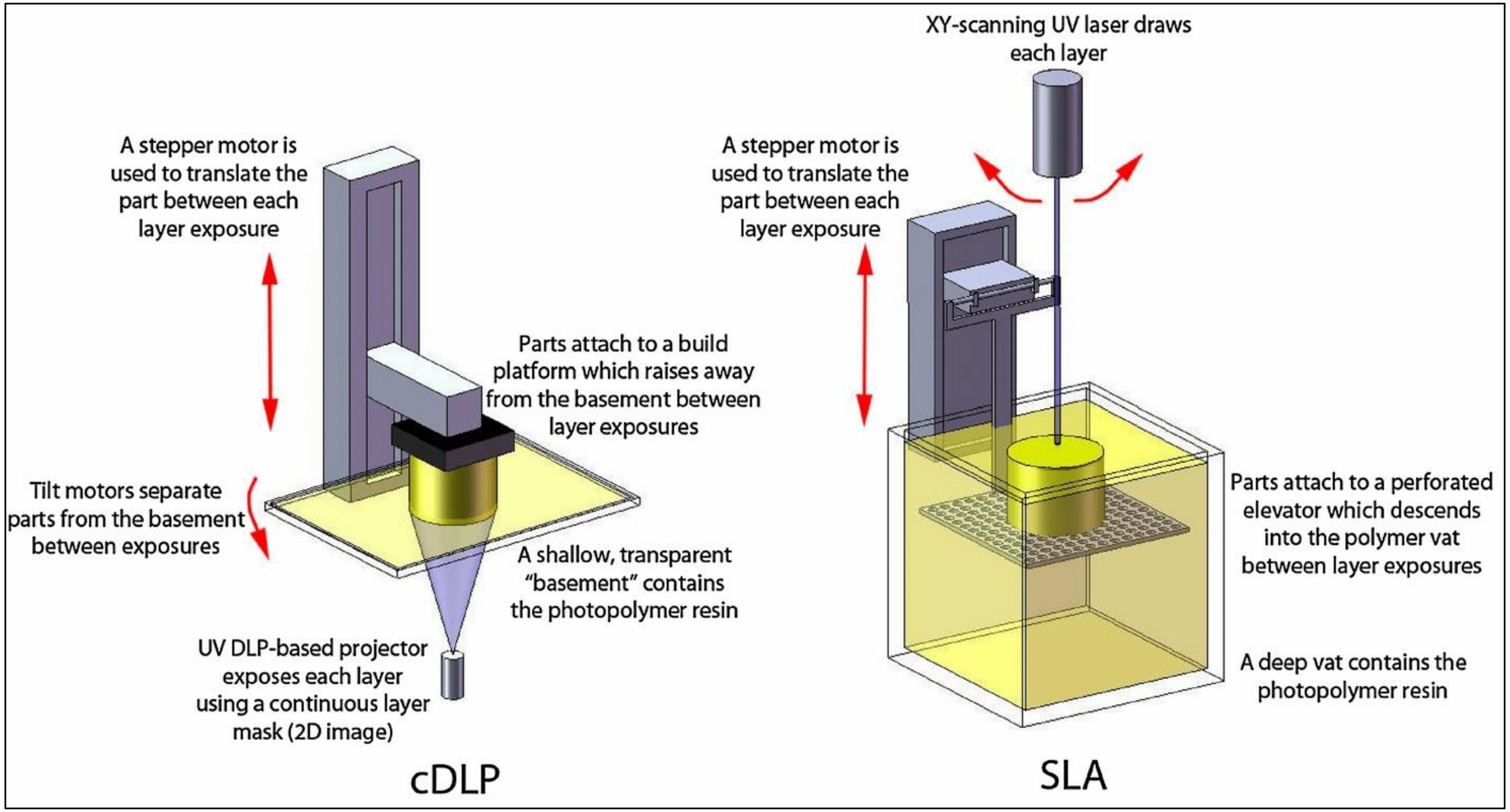
www.hybridmanutech.com

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 (BJ), Selective Laser Sintering (SLS), Stereolithography (SLA), Digital Light Processing (DLP), Laminated Object Manufacturing (LOM)

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

A. Zocca,, P. Colombo, C.M. Gomes, J. Guenster., “Additive Manufacturing of Ceramic-Based Materials,” J. Am. Ceram. Soc., ***98*** *(2015) 1983–2001*

Vat photo-polymerization (SLA/DLP)



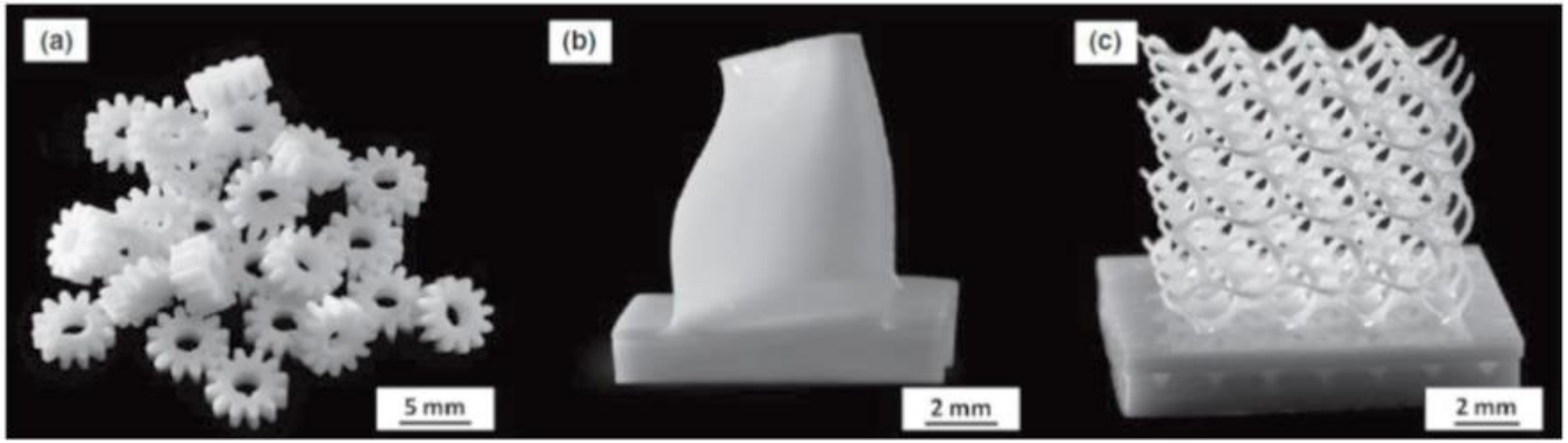
- *Basic working principle*: selective curing (cross-linking) of a polymeric resin by means of an energy source (UV or visible light) – bottom-up or top-down geometries are possible
- Note: continuous printing is possible

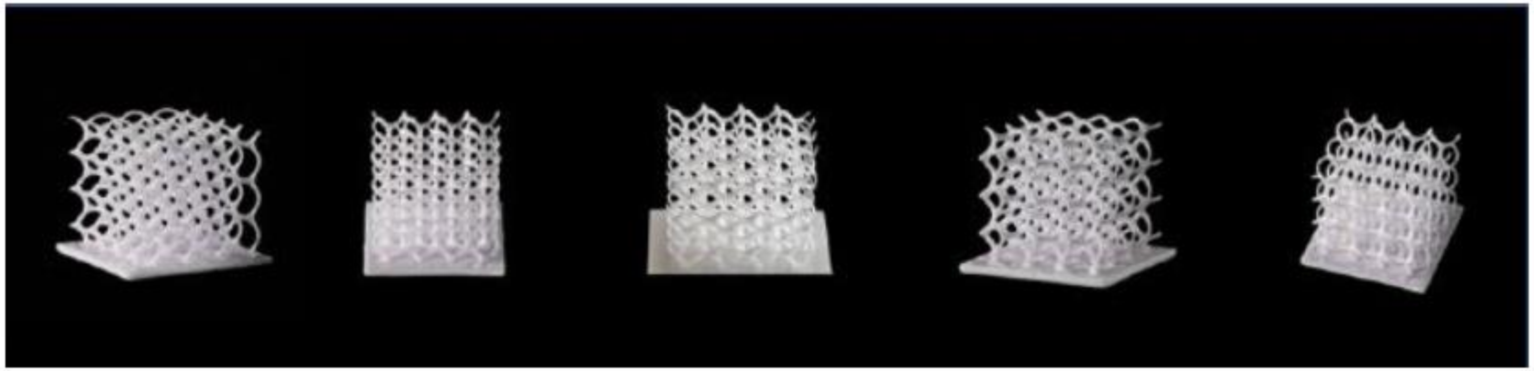
DOI: 10.1088/1758-5082/6/1/015003

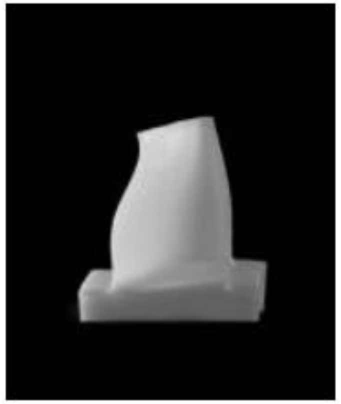
- A typical SLA/DLP mixture contains:

  1) Photo-curable monomers or oligomers; 2) Photo-initiator; 3) Photo-absorber; 4) Diluent (often reactive); 5) Ceramic powders or Ceramic Precursors; 6) Additives

- Polymer suspensions containing 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
- Problems with radiation scattering of particles (index matching) and absorbance (SiC, Si_3N_4)
- Problems in efficient dispersion of particles (non-aqueous medium)

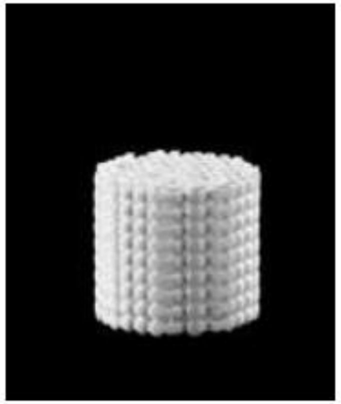






Al_2O_3

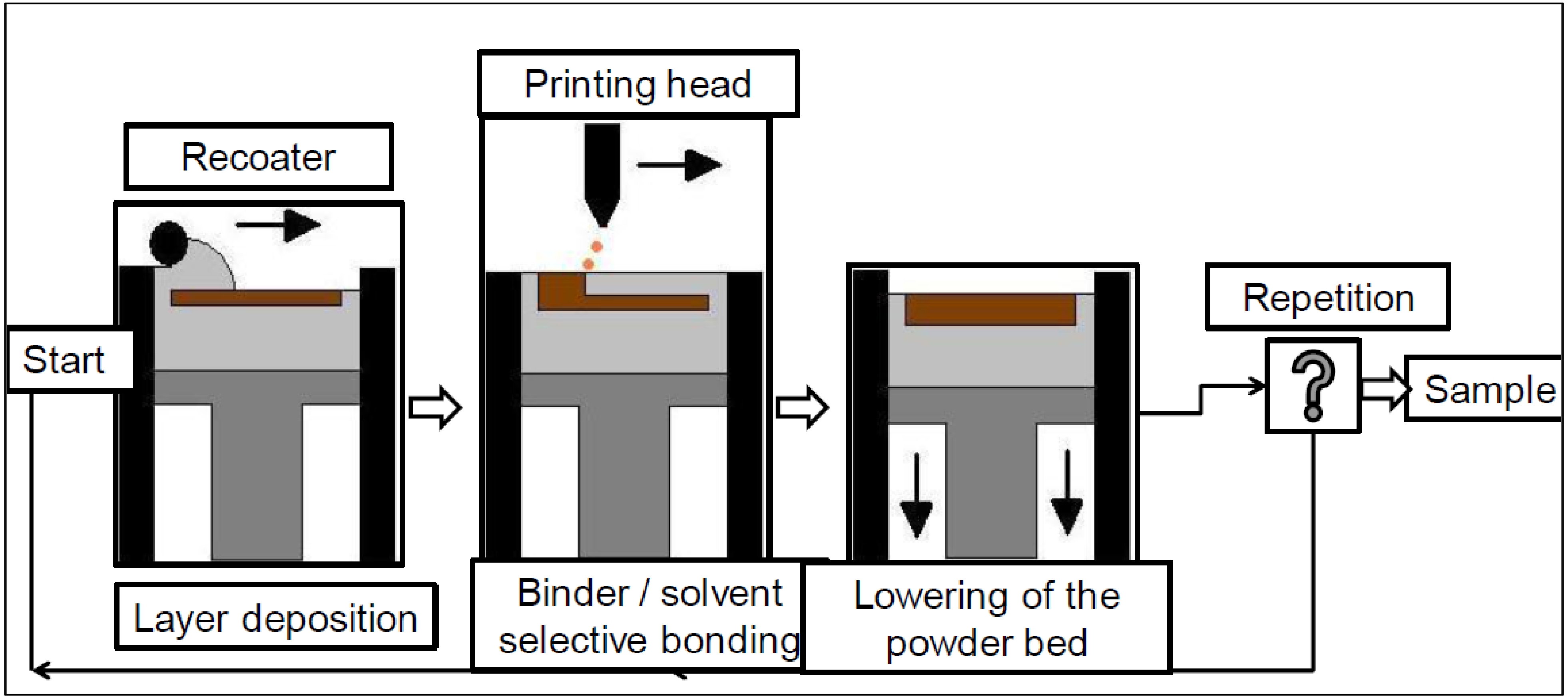
ZrO_2



$Ca_3(PO_4)_2$

www.lithoz.com

Binder Jetting (BJ)



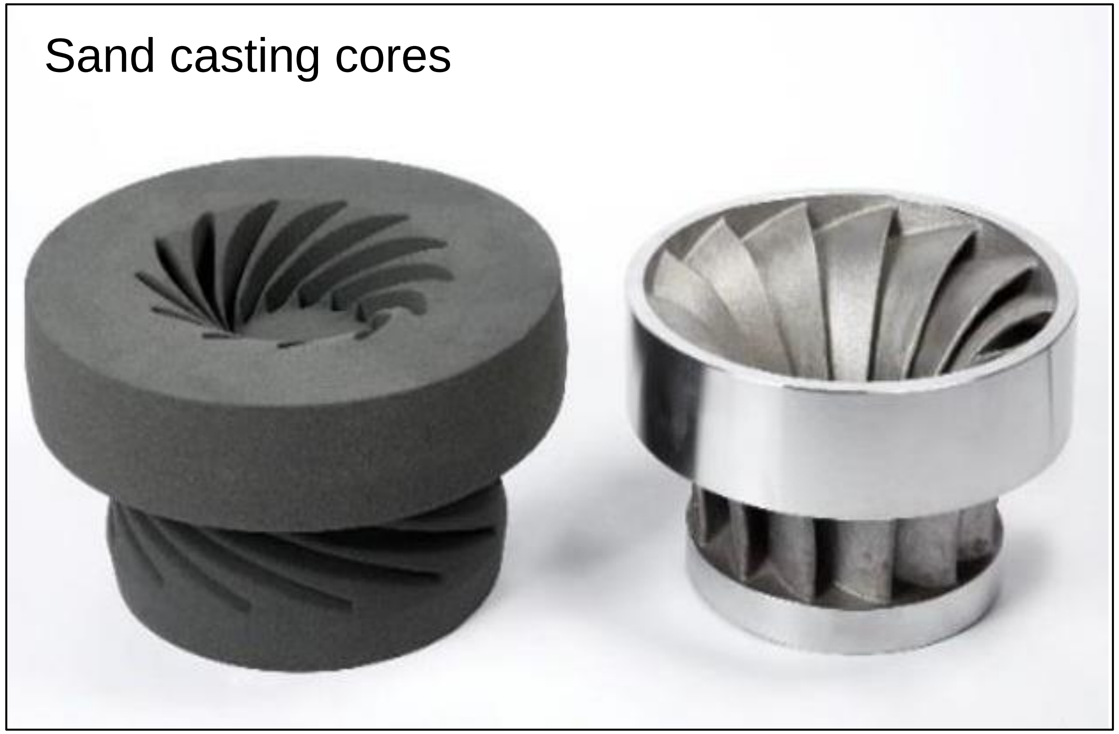
- *Basic working principle*: a liquid bonding agent is selectively deposited to join powders deposited layer-by-layer to form a powder bed
- Flowability of the powders is very important (fine powders (< 20 µm) tend to flow poorly, especially ceramic ones)
- Very large scale printing is possible

Choice of Binder

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

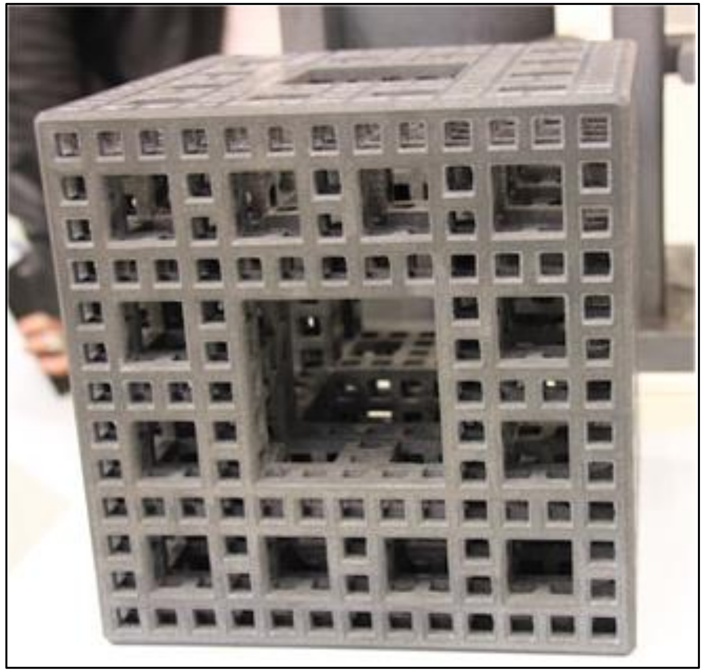
1) The printing liquid is a solvent in which a polymer is dissolved
2) The printing liquid is a pure solvent, and a polymeric binder powder is mixed within the ceramic powder
3) The printing liquid (typically inorganic, or simply water) induces a setting reaction in the ceramic material

https://www.voxeljet.com/

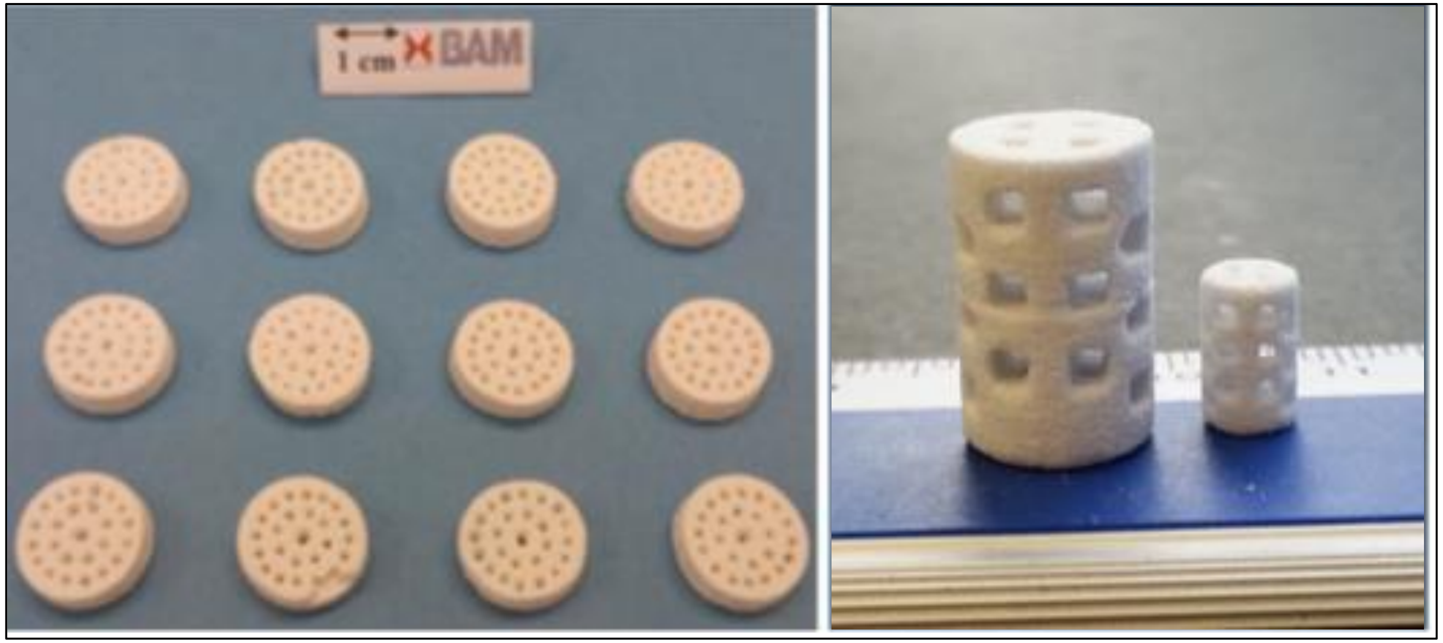


Sand casting cores

Wikimedia Commons

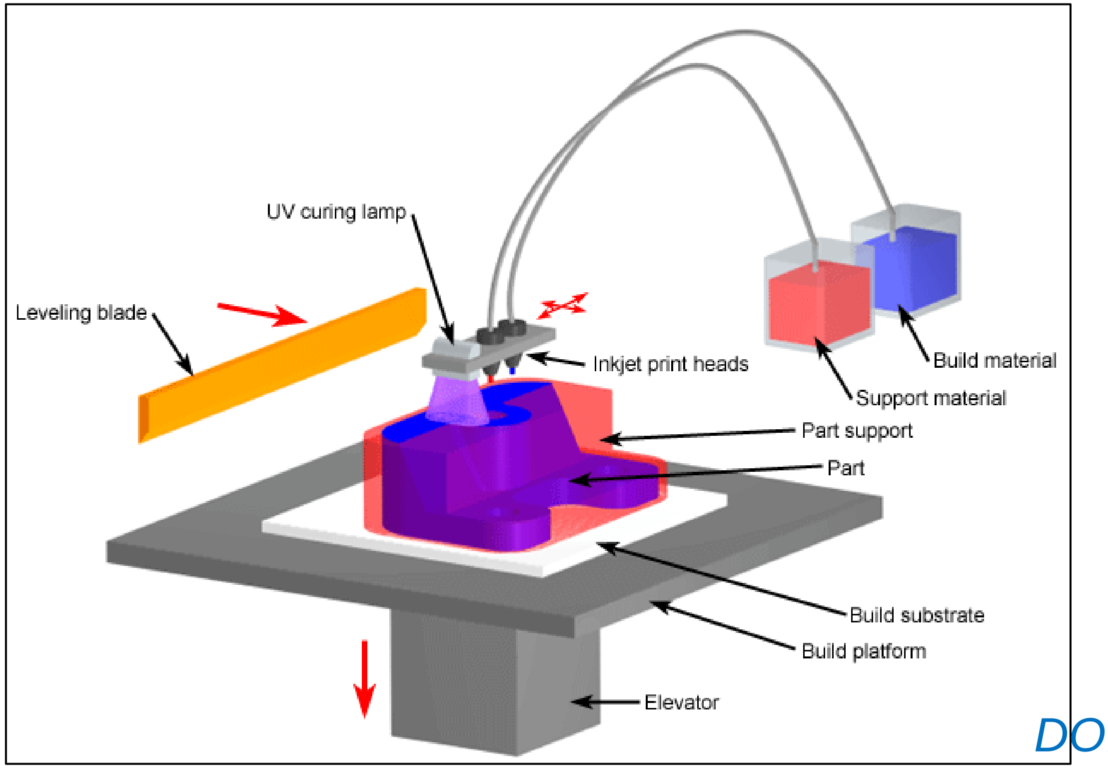


Schunk IntrinSiC® (Si infiltration)



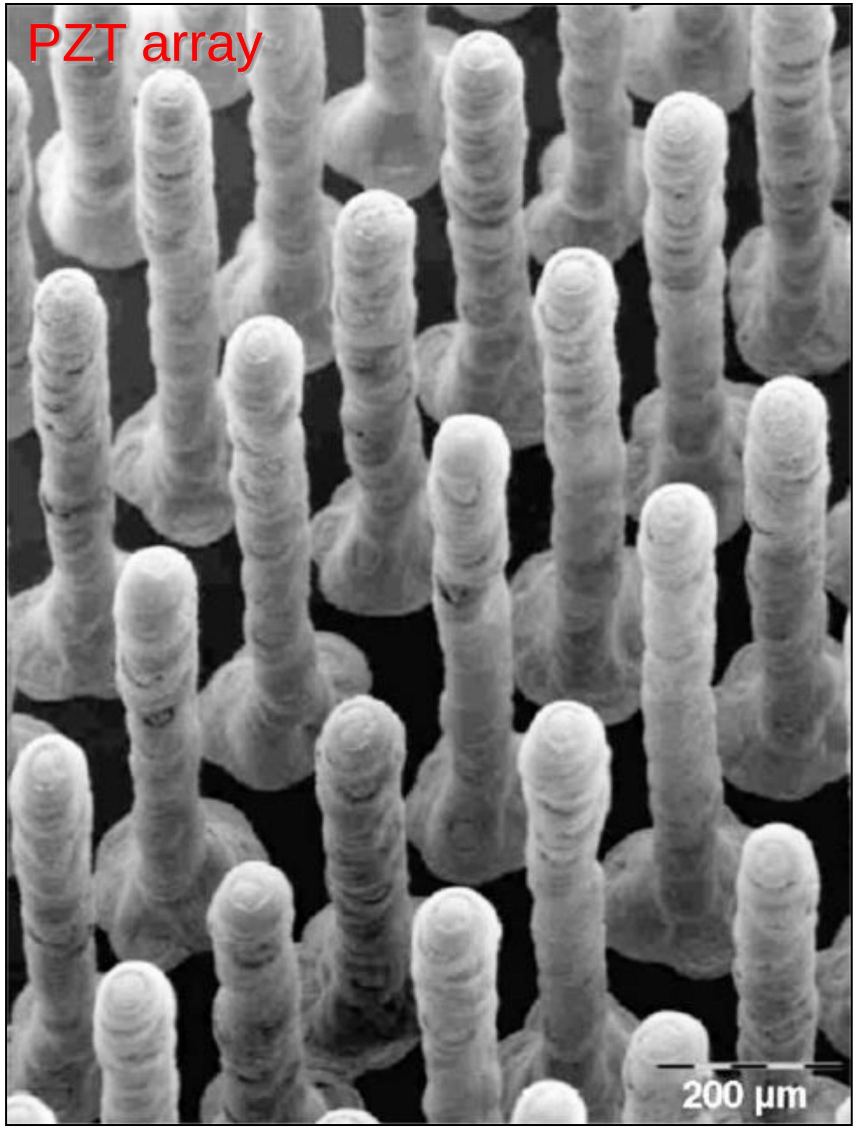
Bioceramics

Inkjet Printing (IP)

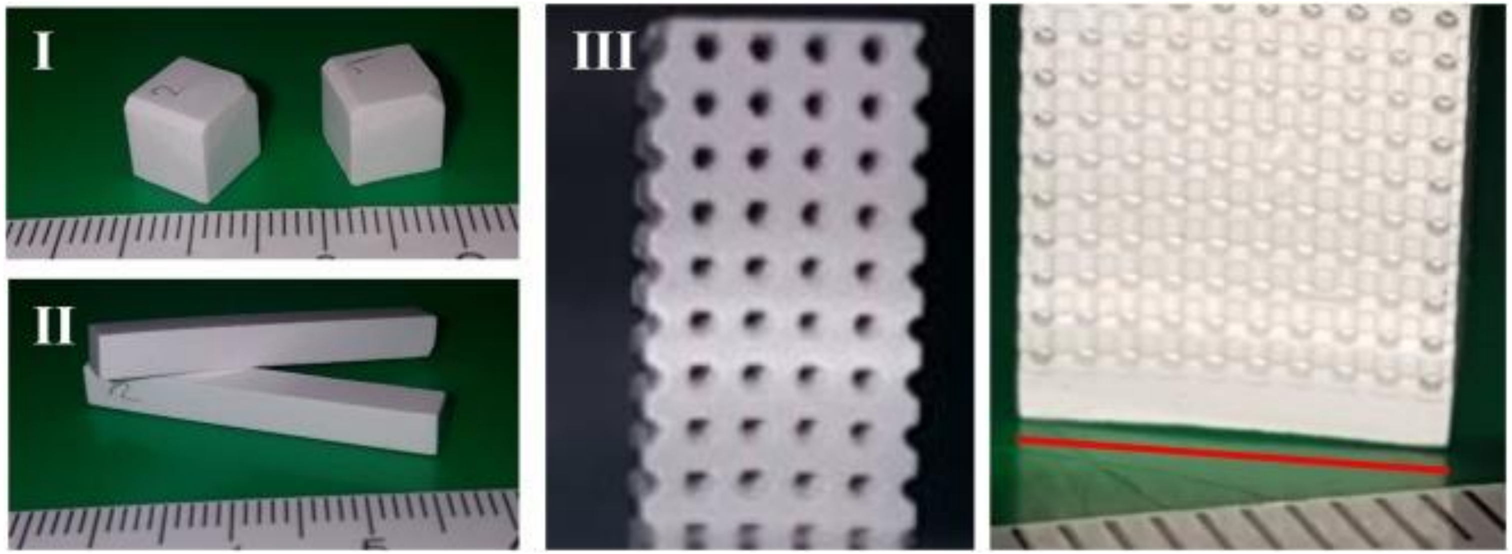


DOI: 10.3844/ajassp.2019.244.272

- *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, and 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
- Use of nano-sized particles based inks (Xjet, IL)
- See also Thermoplastic 3D-Printing (T3DP, IKTS) for micron-sized particles



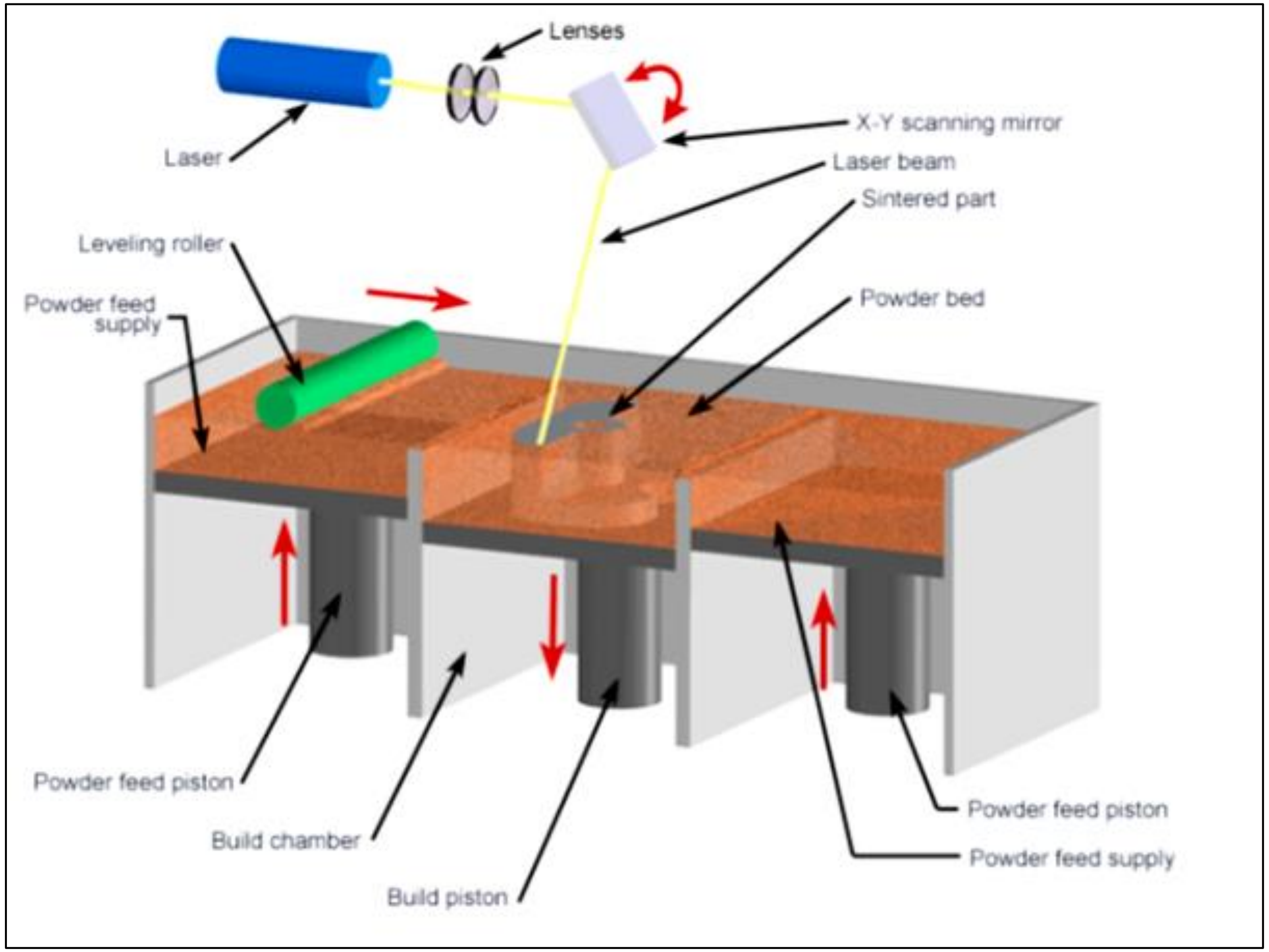
R. Noguera et al., "3D fine scale ceramic components formed by ink-jet prototyping process," J. Eur. Ceram. Soc., ***25*** *(2005) 2055-2059*



E. Schwarzer et al., "Process development for additive manufacturing of functionally graded alumina toughened zirconia components intended for medical implant application," J. Eur. Ceram. Soc., ***39*** *(2019) 522-530*

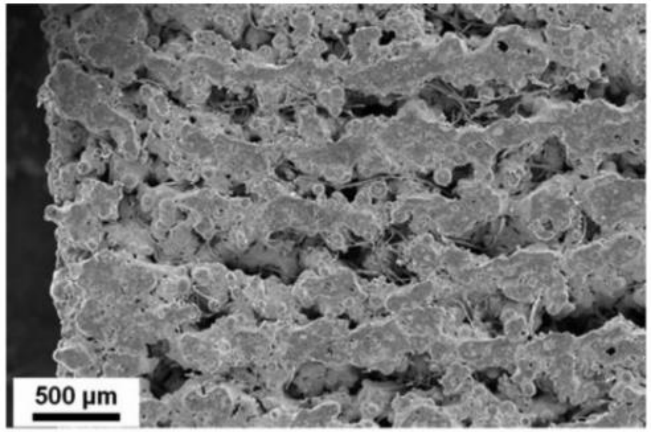
- Multicomponent objects possible
- Graded structures possible
- Some limitations on shapes and aspect ratios exist with this technology

Powder Bed Sintering/Melting) (SLS/SLM)

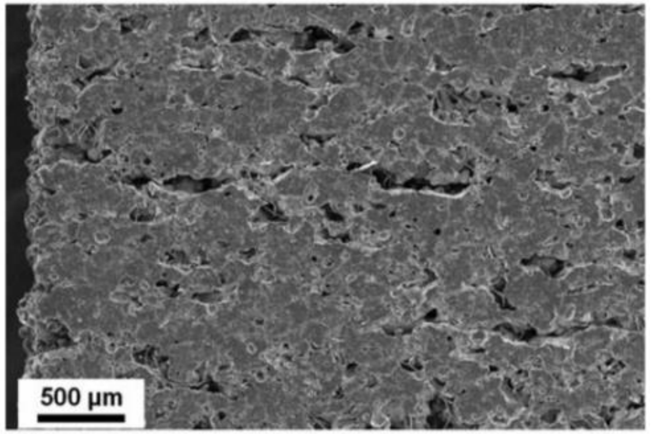


www.custompartnet.com

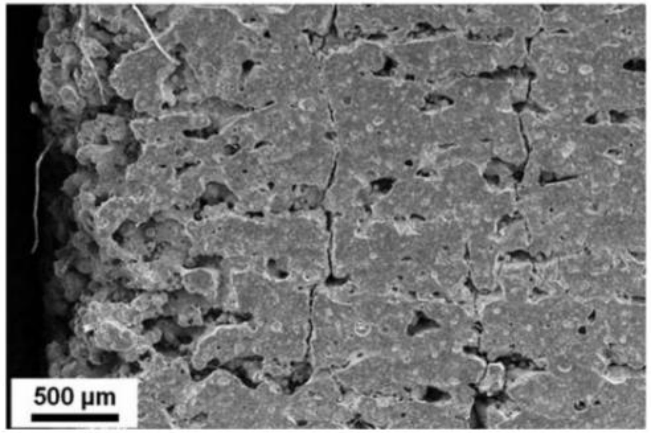
- *Basic working principle*: selective sintering/melting of a powder bed by means of an energy source: 1) Laser → Selective laser sintering/melting (SLS/SLM); 2) Electron beam → Electron beam melting (EBM)
- Very difficult to obtain defect-free ceramic parts by SLS/SLM



(a)



(b)

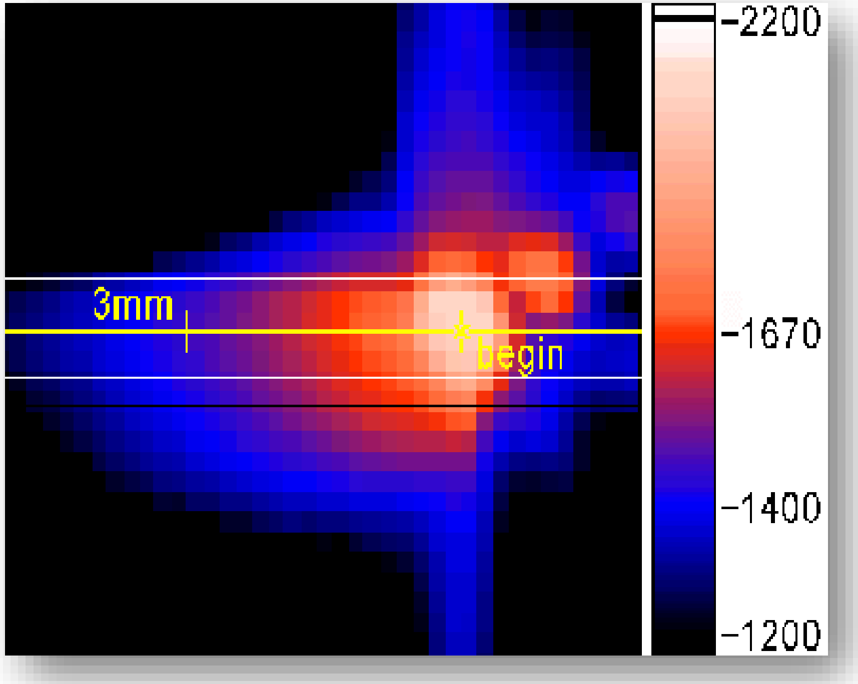


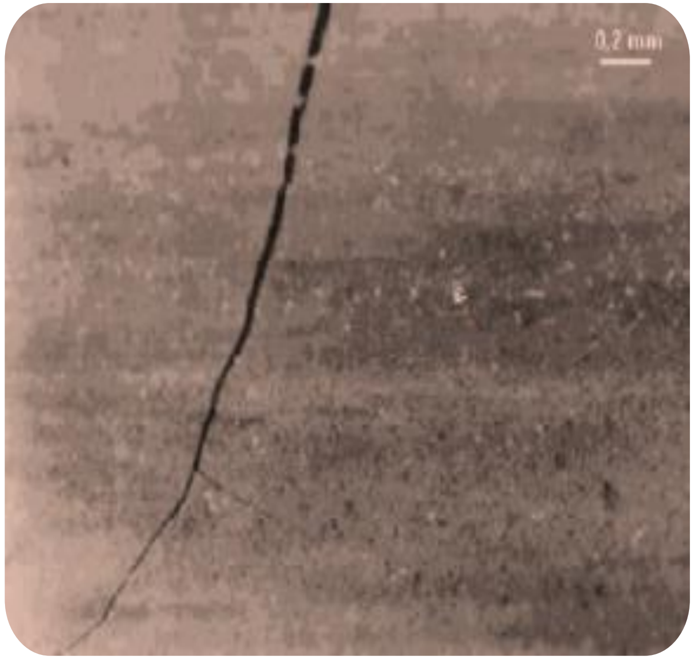

Pure alumina parts processed by SLM

*E. Juste, F. Petit, F., V. Lardot, & F. Cambier, "Shaping of ceramic parts by selective laser melting of powder bed," J. Mater. Res., **29** (2014) 2086-2094*

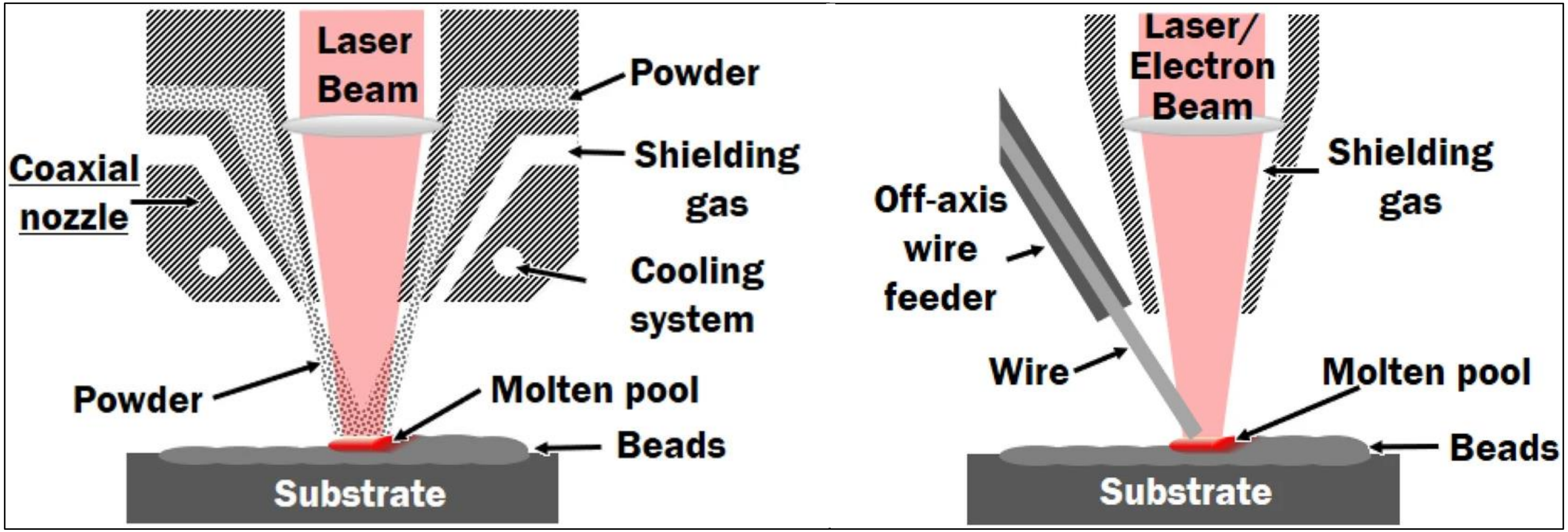
Issues

- 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





Directed Energy Deposition (DED)

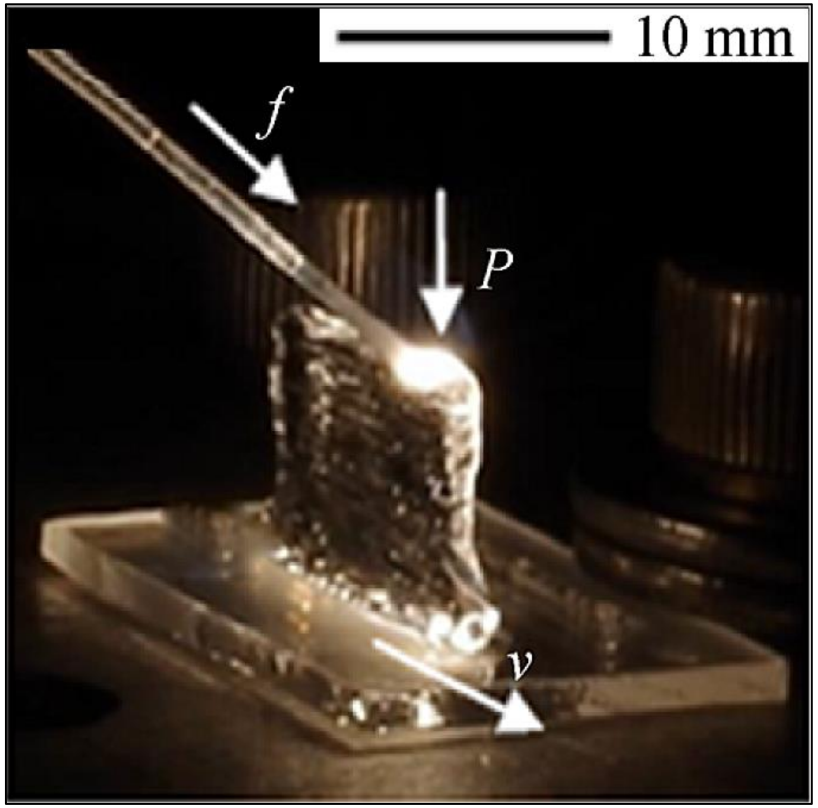


DOI: 10.1007/s40684-020-00302-7

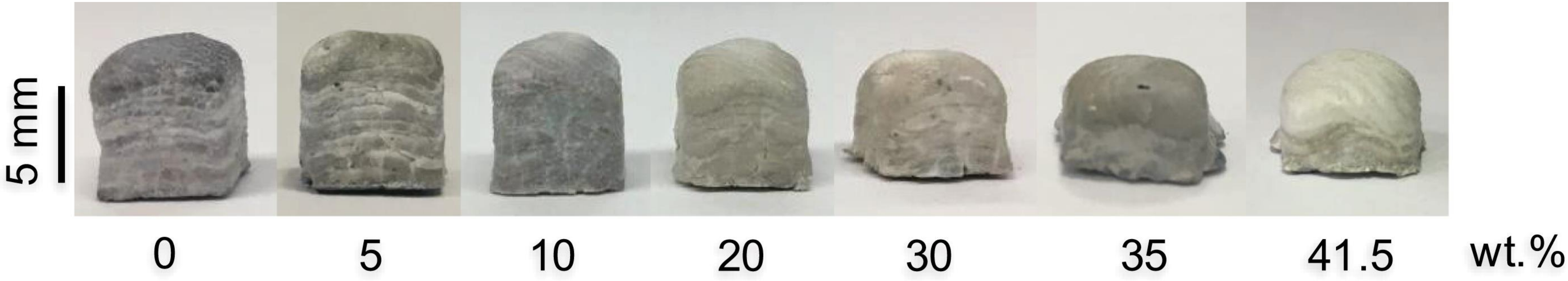
- *Basic working principle*: selective sintering/melting of a ceramic powder/wire by means of an energy source (laser)

Issues

1) High sintering and melting temperatures (better success with glass rods/fibers)
2) Very difficult to obtain defect-free ceramic parts → thermal shock due to fast local cooling (poor resistance to thermal shock of ceramics; preheating to reduce thermal shock is possible but complicated)
3) Difficulty in controlling microstructure (segregation at grain boundaries for multicomponent ceramics)



D. Zhang, X. Liu, J. Qiu, "3D printing of glass by additive manufacturing techniques: a review," Front. Optoelectron., ***14*** *(2021) 263–277*

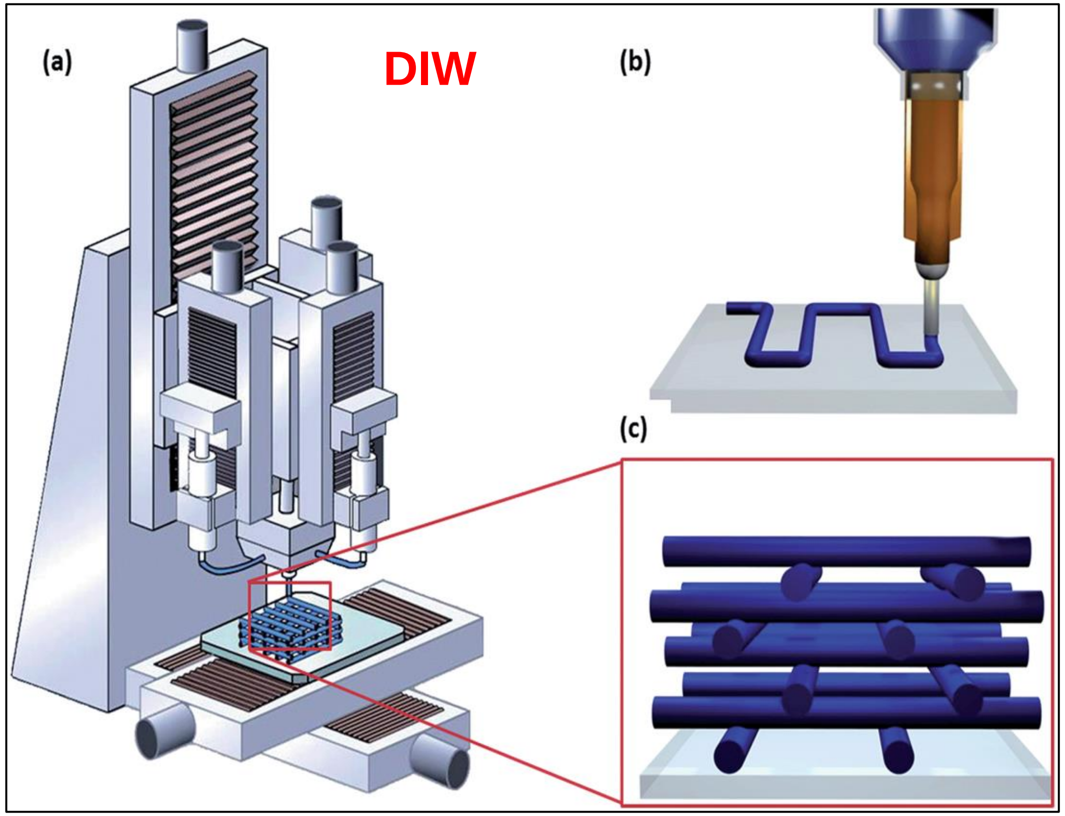


DED-fabricated ZTA parts with different levels of ZrO_2 contents

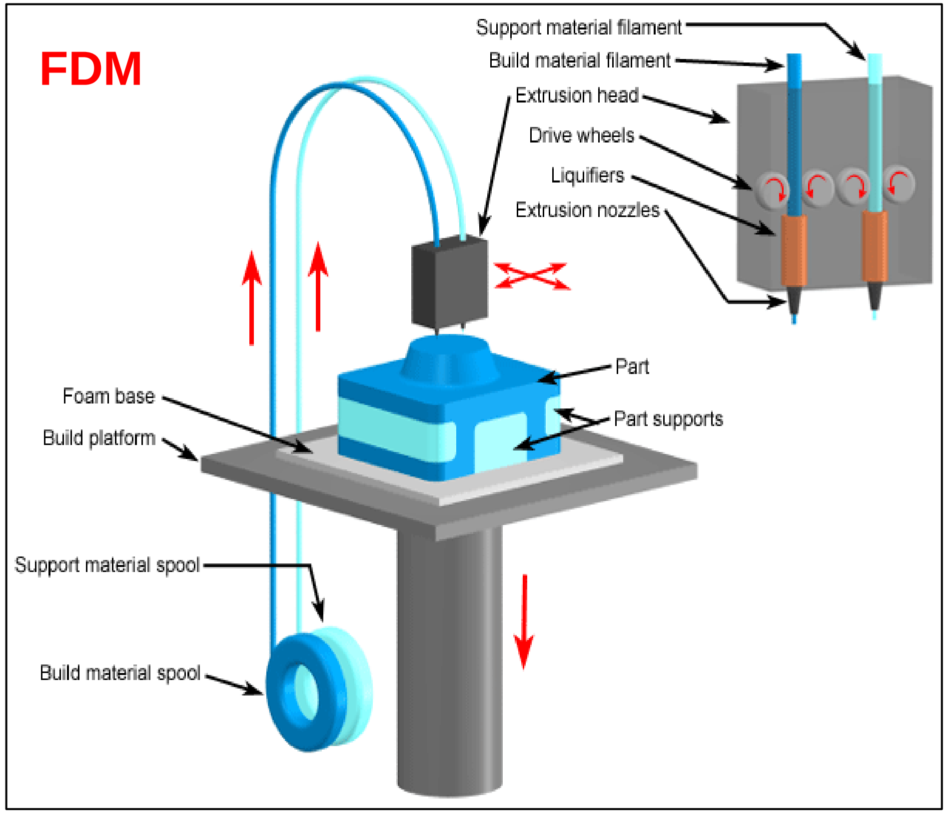
*Y. Hu, H. Wang, W. Cong and B. Zhao, "Directed Energy Deposition of Zirconia-Toughened Alumina Ceramic: Novel Microstructure Formation and Mechanical Performance," J. Manuf. Sci. Eng., **142** (2020) 021005*

*D. Peters, J. Drallmeier, D.A. Bristow, R.G.Landers, E. Kinzel, "Sensing and control in glass additive manufacturing," Mechatronics, **56** (2018) 188-197*

Material Extrusion (DIW, FDM)



DOI: 10.1016/j.reactfunctpolym.2016.04.010

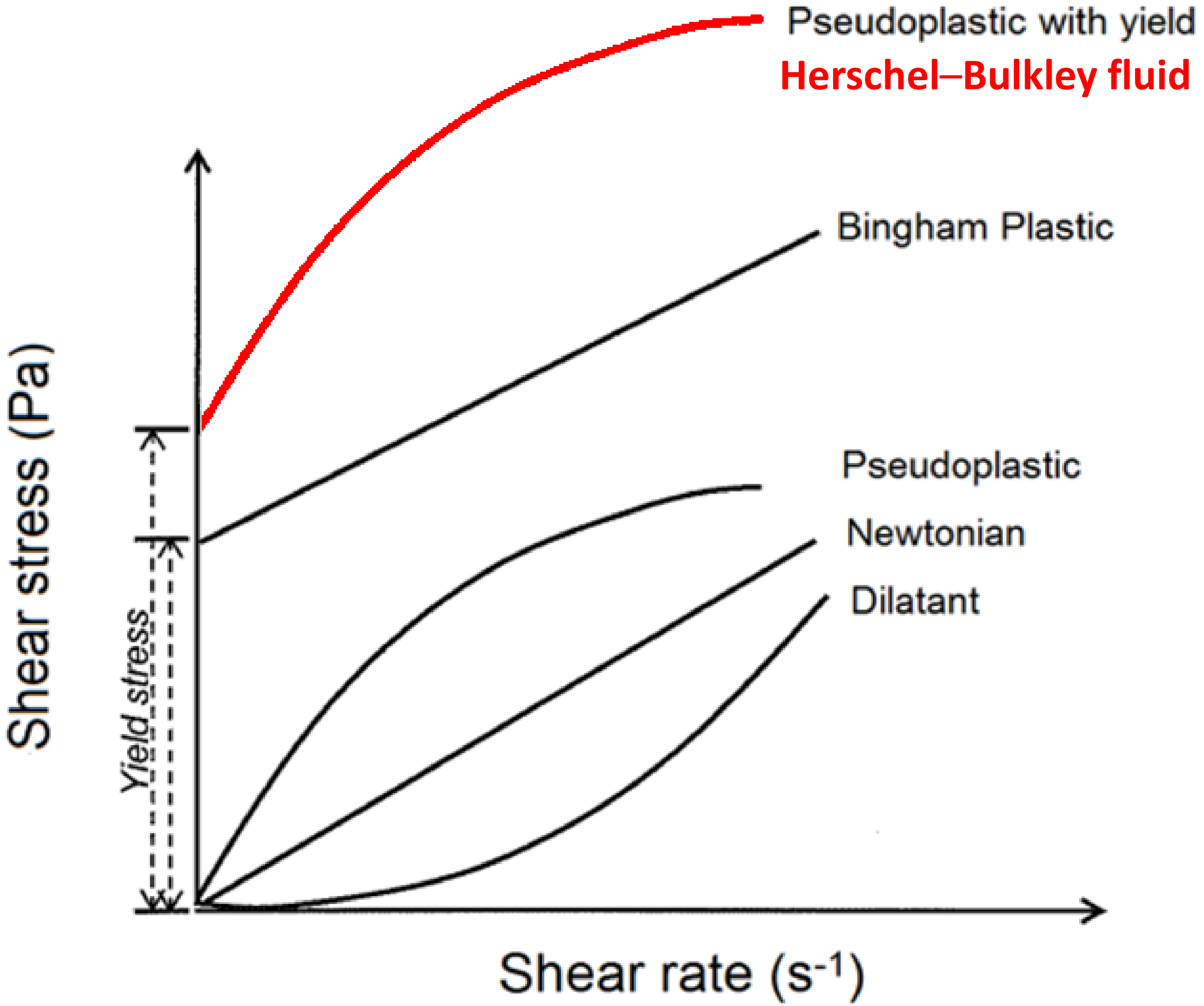


DOI: 10.32570/ijofe.851257

- *Basic working principle*: 1) selective deposition of a paste extruded through a nozzle (also commonly named Robocasting); 2) melting of a filament (or pellets) 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

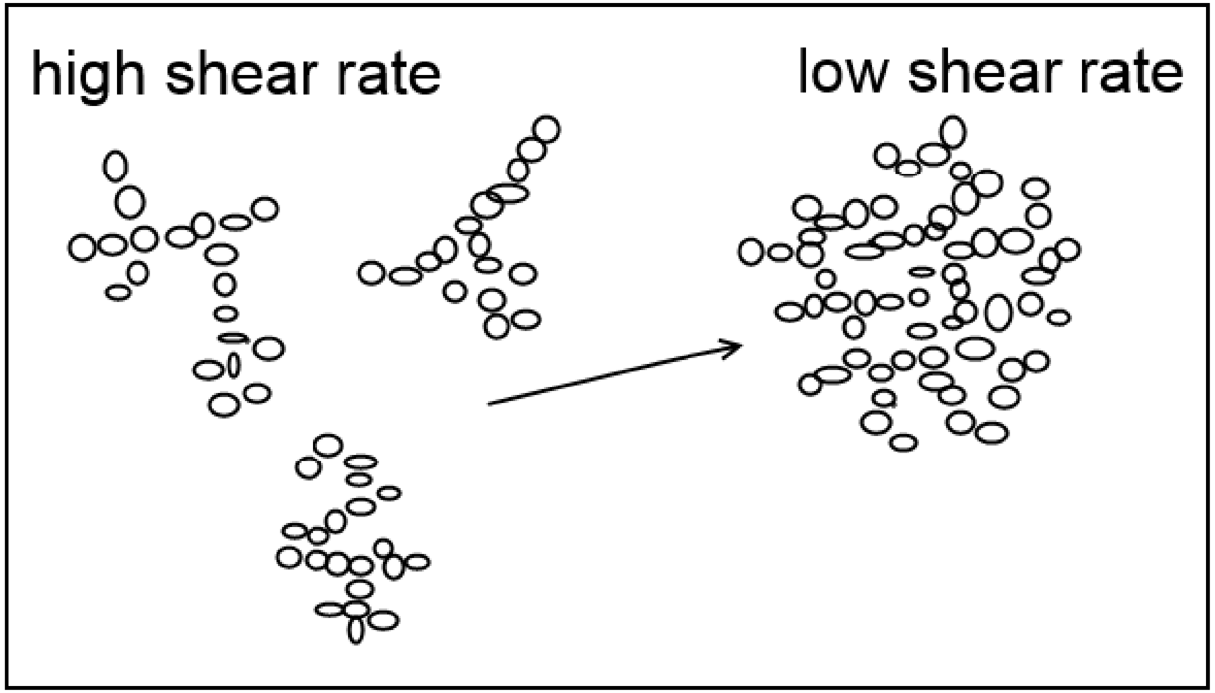
- → pseudoplastic behavior with yield stress (Herschel–Bulkley fluid)
- → strong physical (reversible) gel

DOI: 10.1016/0301-7516(96)00009-9

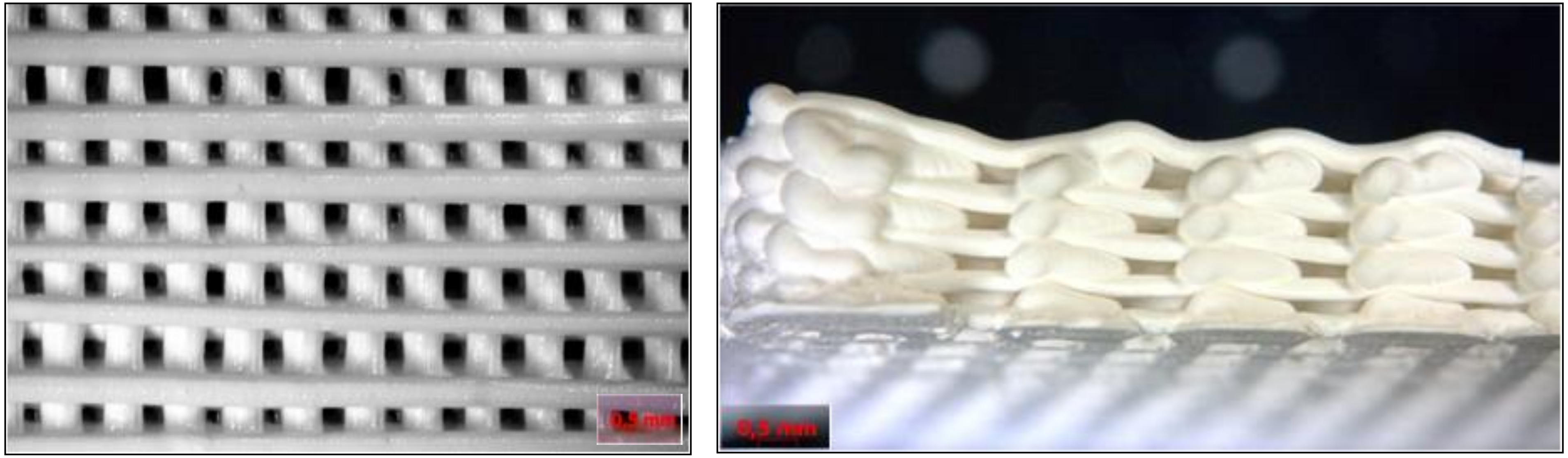
Rheological design of the ink

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



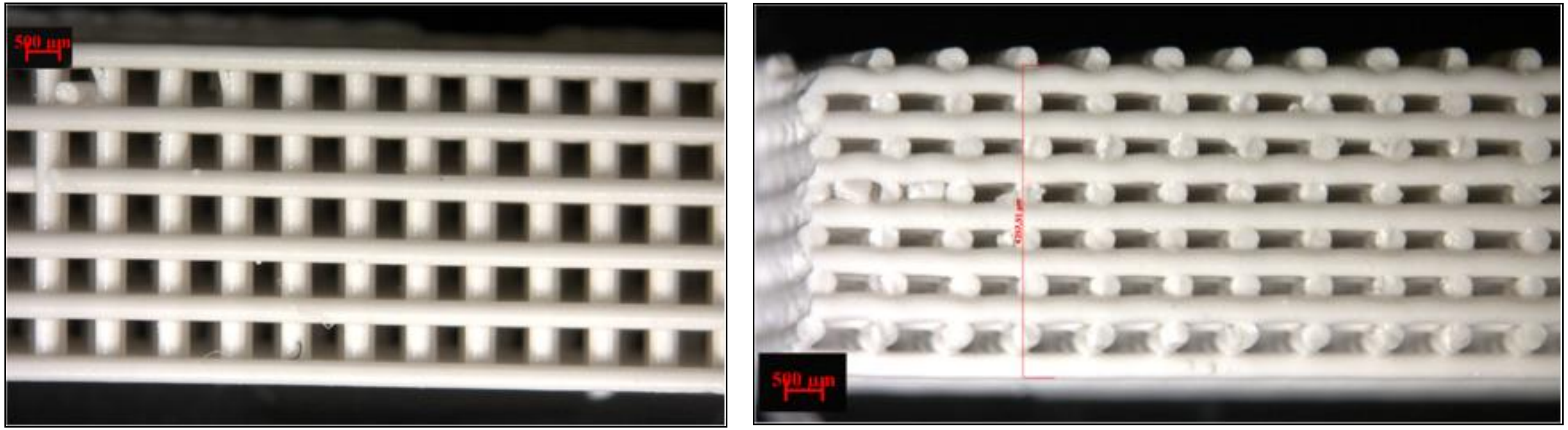
Fumed silica forms a reversible gel with pseudoplastic rheology



X-Y plane

Z axis

Incorrect ink design → sagging



X-Y plane

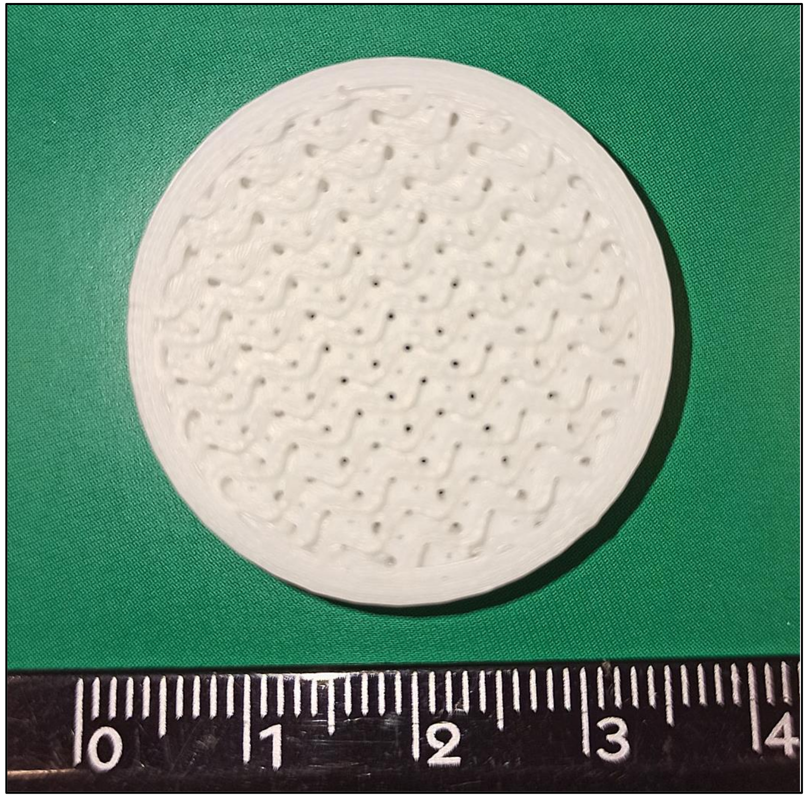
Z axis

Correct ink design → spanning features

Ceramic filaments

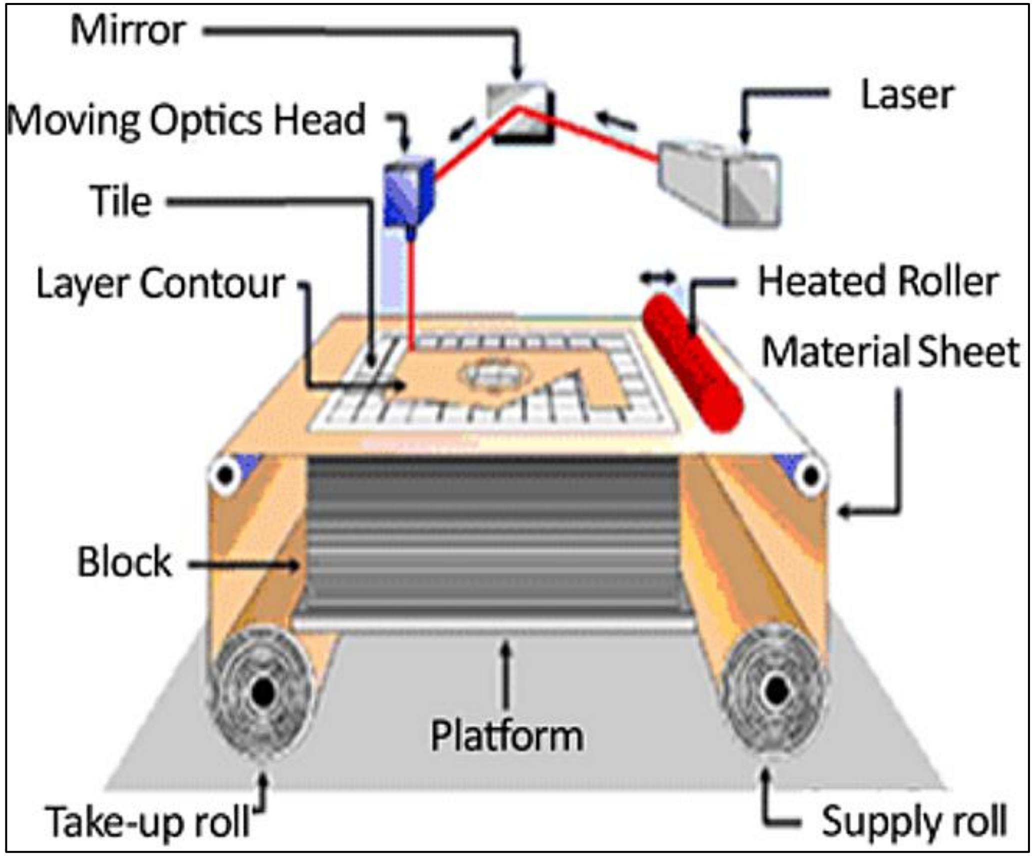
A few companies have started producing filaments for FDM containing ceramic particles:

1. The filaments are more brittle than conventional plastic filaments (modification of printer setup) → problems with spooling and delivery to printer's head
2. Chemical+Thermal debinding possible (20-30 wt% organics)
3. Only few compositions commercially available (Al_2O_3, ZrO_2, $ZrSiO_4$, Borosilicate glass, SiC)



Alumina filter

Laminated Object Manufacturing (LOM)



DOI: 10.1177/1687814018822880

- *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,

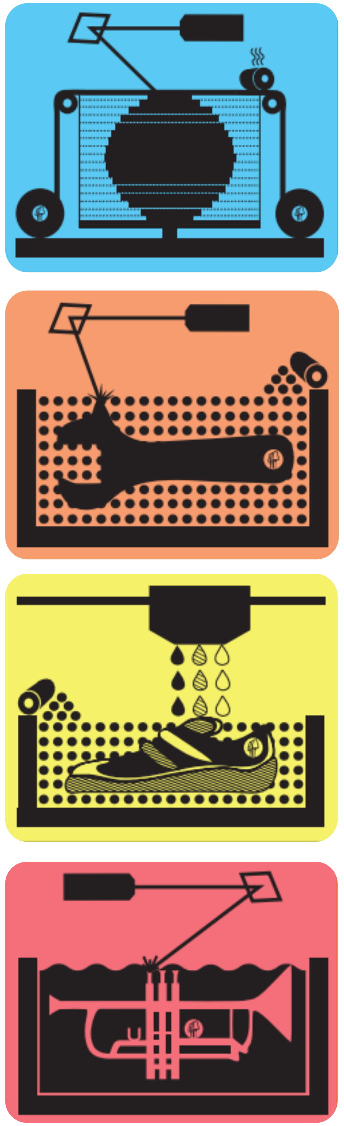
b) Al_2O_3,

c) LZSA glass-ceramic

d) Si–SiC–SiOC–N composite

Travitzky, N., Windsheimer, H., Fey, T. and Greil, P., "Preceramic Paper-Derived Ceramics", J. Am. Ceram. Soc., ***91*** *(2008) 3477-3492*

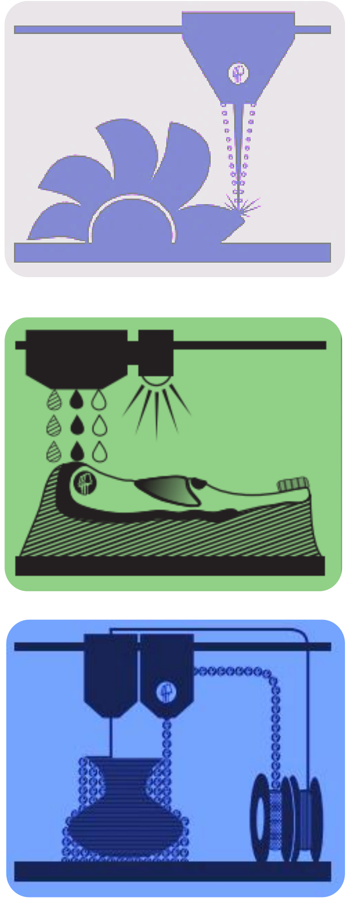
Indirect AM technologies



- ✓ Higher speed
- ✓ Simpler rheology requirements
- ✓ Higher design flexibility but some limitations in terms of 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

	Plus	Minus
Vat photopolimerization	• Very good resolution (down to 20 µm) • Dense and fine microstructure also for technical ceramics • Ample geometrical flexibility	• Debinding is difficult and long for thick parts • Restricted to wall thickness < 10-20 mm • Needs support structures
Material Extrusion	• Very flexible as material's choice • Can produce from small to very large parts • Potentially fast, depending on the geometry and diameter of the nozzle (0.1 mm to cm) • Dense and fine microstructure also for technical ceramics	• Limited geometrical flexibility • Surface quality depends on the stacking of the filaments
Material Jetting	• Dense and fine microstructure also for technical ceramics • Potential for multi-material parts • Good resolution (< 100 µm)	• Potential problems with clogging of the printing head • Slow for large parts • Needs support material
Binder Jetting	• Fast for medium-large areas • Flexible, easy to use with new materials	• Medium resolution (100-200 µm) • Cannot produce a dense and fine microstructure for technical ceramics

Technology comparison 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** (BJ, 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

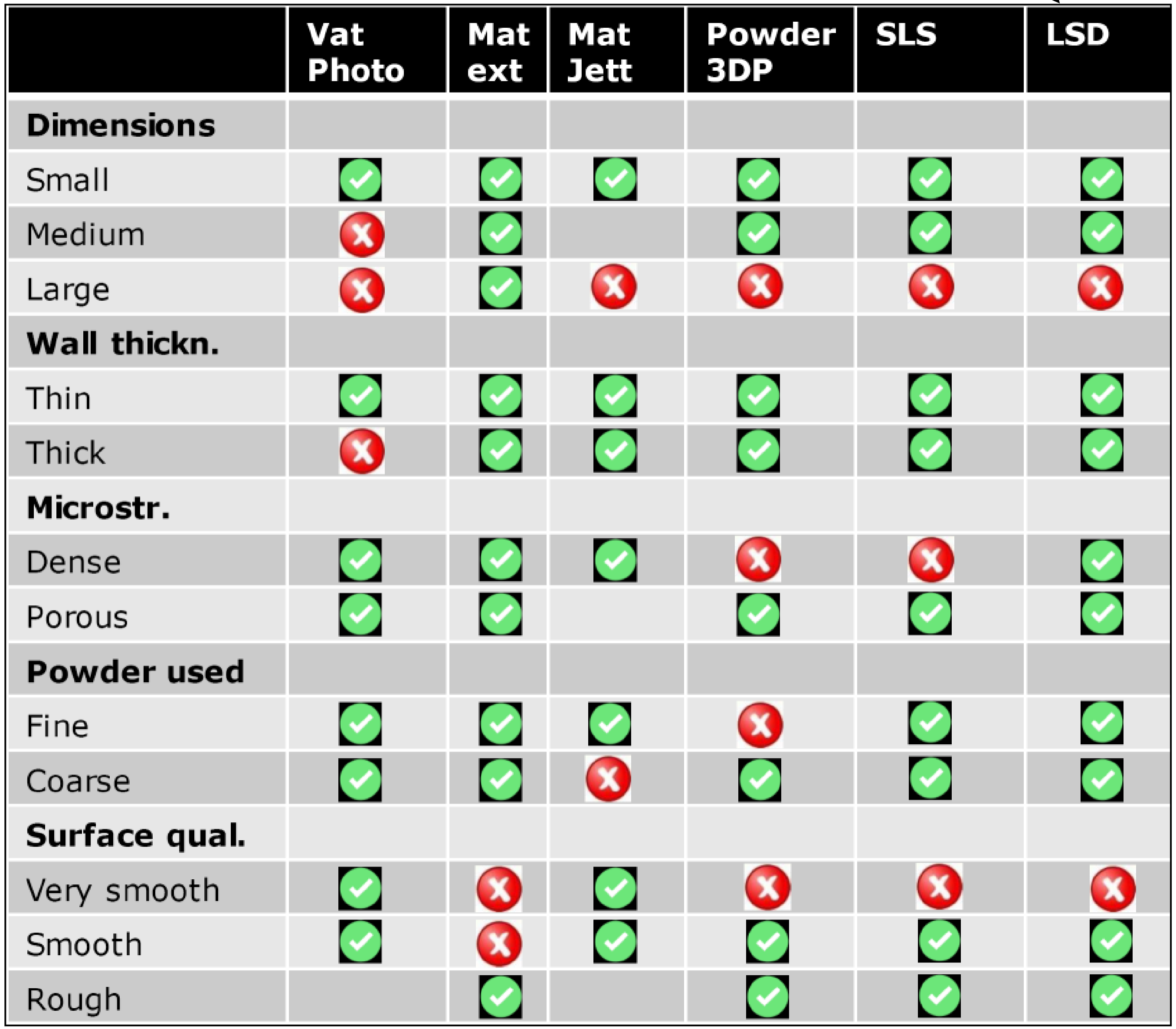
- Fine (< 20 µm, often < 1 µm)
- Coarse (20 – 200 µm)

Surface roughness/quality

- Very smooth (few µm)
- Smooth (tenths of µm)
- Rough (hundreds of µm)

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

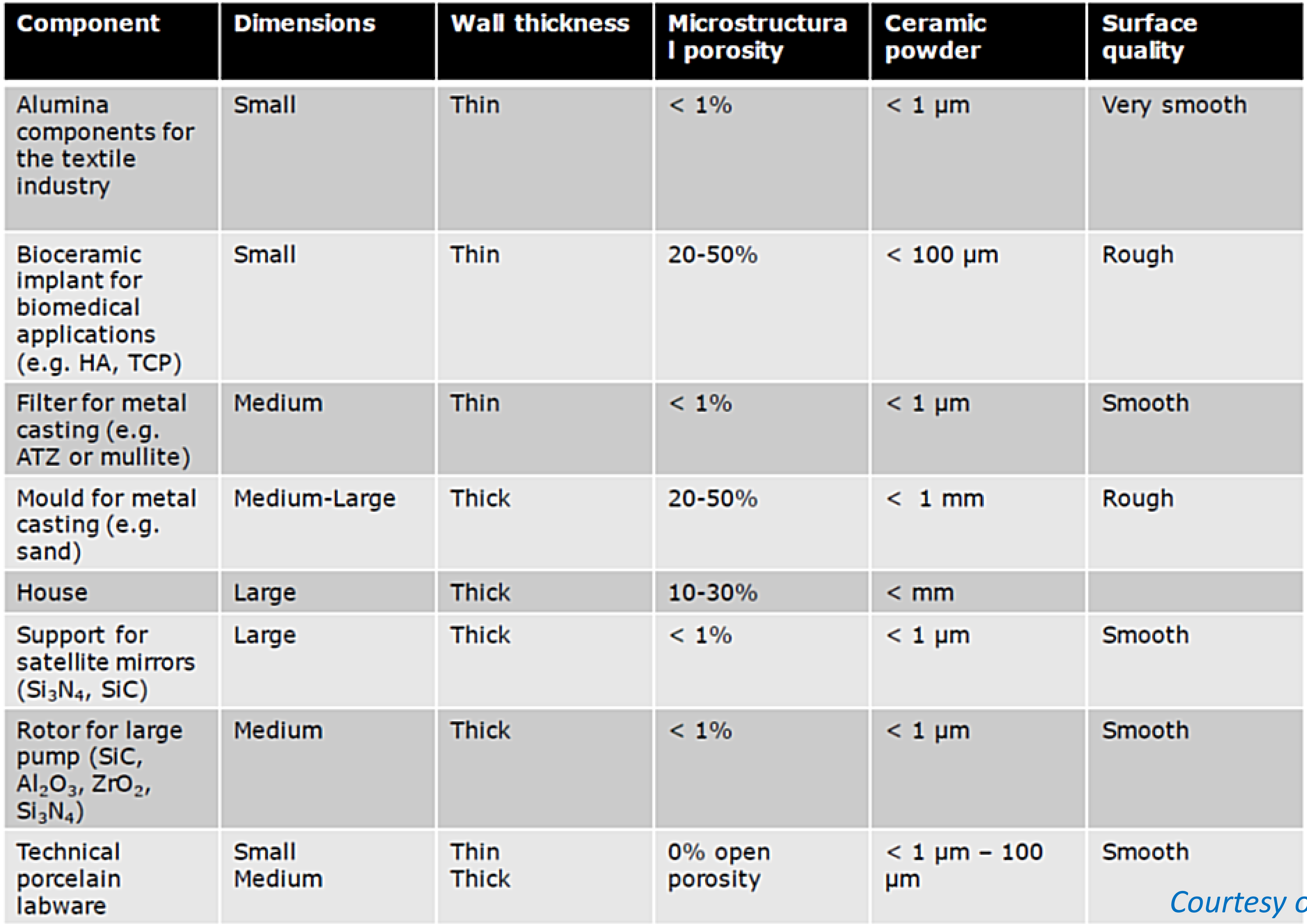
Layerwise slurry deposition



	Vat Photo	Mat ext	Mat Jett	Powder 3DP	SLS	LSD
Dimensions						
Small	✓	✓	✓	✓	✓	✓
Medium	✗	✓		✓	✓	✓
Large	✗	✓	✗	✗	✗	✗
Wall thickn.						
Thin	✓	✓	✓	✓	✓	✓
Thick	✗	✓	✓	✓	✓	✓
Microstr.						
Dense	✓	✓	✓	✗	✗	✓
Porous	✓	✓		✓	✓	✓
Powder used						
Fine	✓	✓	✓	✗	✓	✓
Coarse	✓	✓	✗	✓	✓	✓
Surface qual.						
Very smooth	✓	✗	✓	✗	✗	✗
Smooth	✓	✗	✓	✓	✓	✓
Rough		✓		✓	✓	✓

Courtesy of A. Zocca, BAM

AM of ceramics: case studies



Component	Dimensions	Wall thickness	Microstructural porosity	Ceramic powder	Surface quality
Alumina components for the textile industry	Small	Thin	< 1%	< 1 µm	Very smooth
Bioceramic implant for biomedical applications (e.g. HA, TCP)	Small	Thin	20-50%	< 100 µm	Rough
Filter for metal casting (e.g. ATZ or mullite)	Medium	Thin	< 1%	< 1 µm	Smooth
Mould for metal casting (e.g. sand)	Medium-Large	Thick	20-50%	< 1 mm	Rough
House	Large	Thick	10-30%	< mm	
Support for satellite mirrors (Si_3N_4, SiC)	Large	Thick	< 1%	< 1 µm	Smooth
Rotor for large pump (SiC, Al_2O_3, ZrO_2, Si_3N_4)	Medium	Thick	< 1%	< 1 µm	Smooth
Technical porcelain labware	Small Medium	Thin Thick	0% open porosity	< 1 µm – 100 µm	Smooth

Courtesy of A. Zocca, BAM

AM of ceramics: case studies

<table>
<tr><th>Component</th><th>Dimensions</th><th>Wall thickness</th><th>Microstructural porosity</th><th>Ceramic powder</th><th>Surface quality</th></tr>
<tr><td>Alumina components for the textile industry</td><td colspan="5">1) Vat photopolymerization</td></tr>
<tr><td>Bioceramic implant for biomedical applications (e.g. HA, TCP)</td><td colspan="5">Powder-based 3DP; Vat photopolymerization; Material extrusion; Material Jetting (order depends on part specs)</td></tr>
<tr><td>Filter for metal casting (e.g. ATZ or mullite)</td><td colspan="5">1) Material Extrusion; 2) Vat photopolymerization;</td></tr>
<tr><td>Mould for metal casting (e.g. sand)</td><td colspan="5">1) Powder-based 3DP</td></tr>
<tr><td>House</td><td colspan="5">1) Material extrusion (extrusion of concrete)</td></tr>
<tr><td>Support for satellite mirrors (Si_3N_4, SiC)</td><td colspan="5">? New technologies needed</td></tr>
<tr><td>Rotor for large pump (SiC, Al_2O_3, ZrO_2, Si_3N_4)</td><td colspan="5">1) LSD</td></tr>
<tr><td>Technical porcelain labware</td><td colspan="5">LSD; Material extrusion; Vat photopolymerization (order depends on part specs)</td></tr>
</table>

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**

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

  - **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: 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: challenges

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

Powder beds:

- 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

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

- **debinding**
- sintering / infiltration

Other concerns

- Process robustness / Repeatability
- High yields from different machines with different batches of raw materials with different operators on different days…!
- Operator proof!
- “Insensitivity” to natural materials
- Inspection methods for “few” types of process defects (e.g. interlayer weaknesses)
- Rate of additive printing in itself (thickness of layers versus resolution? How many parts on a bed versus resolution?)
- Post processing (debinding and fire: time and capital investment towards a slower process)
- Can one or a small number of technologies be sufficiently flexible to address a wide spectrum of components?
- Current rate of technology development is both a blessing and a curse…!

Powder vs Liquid-based feedstocks for AM of ceramics

Issues with powder-based feedstocks → <u>advantages of all liquid feedstocks</u>

1) Very viscous slurries (special DLP equipment required → expensive)
2) Light scattering, penetration depth and index matching (vat photopolymerization)
3) Stabilization of particles in non aqueous-medium is difficult
4) Particle size controls nozzle dimension (DIW) → limit in feature size and surface quality
5) Clogging of nozzle (DIW)

Preceramic polymers; Sol-gel solutions; Geopolymers

Issues with all liquid-based feedstocks

1) Not all of the potential all liquid feedstocks (preceramic polymers, sol-gel, geopolymers) can be used with every class of AM technology (~~BJ, FDM, SLS/SLM~~)
2) The compositional range of the resulting ceramics is rather limited for all but sol-gel-based formulations

Nevertheless, all liquid feedstocks have some advantages that can be exploited

*G. Franchin, P. Colombo et al., CJME:AMF, **1** (2022) 100012*

AM of Ceramics: when to use it?

- **AM is more economical** if parts are: complex, small, individual (low batch numbers)
- **Application is suitable for additive manufacturing** if:
  - Parts are critical and expensive
  - Tool costs are high in relation to part price
  - Material costs are high in relation to production costs
  - Ratio of waste material is high within the production process
  - Machining of the parts is difficult
  - Parts are often modified

AM of Ceramics: when to use it?

- **Application is suitable for additive manufacturing** if:
  - Assembling consists of many parts
  - Assembly costs are high
  - More functionalities are required
  - Light weight structures are required
  - Higher efficiency can be realized within the entire value chain
  - For generating new unique customer opportunities

AM of ceramics: future

- Further development of technologies
- High resolution printing (finer details)
- Hybrid technologies (combination of technologies)
- Large scale printing
- Multi-material printing
- Industrialization (e.g. several printers in parallel) → high output
- Selection of most appropriate AM technology for the production of a specific component
- DFAM (Design For Additive Manufacturing) approach

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

Acknowledgements

Dr. Johannes Homa (Lithoz, Vienna, Austria)

Dr. Andrea Zocca (Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany)