Generative Manufacturing of Ceramic Parts "Vision Rapid Prototyping"

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Introduction

When Generative Manufacturing Processes had been introduced to the market in the early 1990s they were called Rapid Prototyping Processes. In the following 15 years they became an important tool especially for the product development of injection molded plastic parts. Based on improved materials and machines, today even final plastic parts can be manufactured (Rapid Manufacturing). Case studies show (www.rtejournal.de, [LENZ04]), that Rapid Manufacturing is about to compete with traditional production processes.

Processes for making metal parts are still under development. Although especially some German developers of Laser Sintering and Laser Melting processes presented impressive case studies on metallic parts for tooling as well as for direct application, there are still some withdraws. The problems of distortion and warping and especially a still unsatisfying surface quality have to be overcome in order to allow a broad industrial use.

Until now, ceramic materials do not play an important role in the field of generative manufacturing. In this context it is very interesting that already in 1993 the US company Soligen presented a process for the manufacturing of ceramic shells for investment casting. It is called DSPC (Direct Shell Production Casting) and will be described in the chapter 3D Printing (below).

After a quite busy period of ceramic research in the mid-1990s the generative community concentrated more on plastic and later on metallic parts.

That is why generative manufacturing today is more or less a vision in the ceramic industry.

Since a couple of years we recognize somewhat of a renaissance. This paper therefore shows which generative processes are available for the application of ceramic materials and which of them are still under development. It aims to discuss the pros and cons and to point out the future perspectives.

Due to the character of a general survey it cannot cover a detailed description of the processes. This gap will be closed by the following relevant reports of the researchers and by some bibliographic recommendations.

1. Generative Manufacturing Processes

Rapid Prototyping (and its applications Rapid Tooling and Rapid Manufacturing) are generally



Figure 1: Generative Fabricated Parts. Model of a Scull, 3D Printing (CP-GmbH, left), Chess Tower (cut away Model, Stereolithography, 3D Systems, right)

regarded as a synonym for additive manufacturing processes whose generic name is generative manufacturing processes.

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The manufacturing is done by joining contoured layers of constant thickness on top of each other. That is why any geometry can be made including the bone structure of the scull shown on Figure 1. It is obviously that it could not be made by milling, by casting or by any other traditional method.

The manufacturing in layers causes a stair stepping effect which is clearly visible on the surface of the parts and which characterizes today's generative manufacturing processes. Generative manufacturing works without product specific tools. Virtual 3D CAD models are directly transformed into physical parts. Thus a complete 3D CAD data set is a precondition for using generative manufacturing processes.

Since the first introduction of generative processes in 1987, over 30 different families of machines have been developed. The most important industrial used processes are listed in
Table 1. Because there is often somewhat of a confusion concerning the indication, the generic
 name and its abbreviation is listed as well as the manufacturer and the brand name.

Commercialized processes preferably work with plastics, some of them additionally with metals.

A summary of the basics of generative fabrication processes can be downloaded from the website: www.fh-aachen.de/Gebhardt.html (follow: "downloads", click: RP-Seminar (english). A comprehensive description of all aspects can be found in the book "Rapid Prototyping" [GEB00].

Process (generic name)	Abbr.	Process Description	Process (brand name)	Abbr.	Manufacturer
Extrusion; Fused Layer Modeling	FLM	Extrusion of thermoplastic Materials	Fused Deposition Manufacturing	FDM	Stratasys
3D-Printing; Three Dimensional Printing	3DP	Joining of powders using binders	3D Printing	3DP	Z-Corp, ProMetal
Laser Sintering	LS SLS	Local melting of thermoplastic Materials	Selective Laser Sintering; Laser Sintering	SLS LS	3D Systems, EOS, Phenix,
Layer Laminate Manufact.	LLM	Joining of foils, e.g. by gluing	Laminated Object Manufacturing	LOM	Cubic Technologies
Stereolithography	SL	Polymerisation of liquid Monomers	Stereolithography	SL	3D-Systems, Objet

Table 1: The most frequently industrially used generative Manufacturing processes, its generic and brand names, abbreviations and manufacturers.

2. Classification of Generative Manufacturing Processes

Seen from the fabrication point of view, it is useful to classify the generative processes due to

Raw- Material		Process (Generic Name)
• Solid: Wire Powde Foil	– ۳ ل	Extrusion 3D-Printing Sintering Layer-Laminate
• Liquid	τ	Stereolithography (Laser/Lamp) PolyJet
 Pasty 	—	Paste Polymerization

Table 2: Relations between Raw Material, Processes and their Generic Names

the state of aggregation of the raw material. **Table 2** shows how the five classical generative processes listed in **Table 1** are linked to these criteria. Looking at a feedstock in solid, fluid or pastry condition all five classic generative processes are covered.

Non generative Processes - Layer Milling

"Rapid" has become a synonym for progress and today it is adapted even by non generative techniques. Especially milling, which is a subtractive fabrication process, often is called rapid as well. Looking at the details, one can consider that for example Layer Laminate Processes are not pure generative, but combined subtractive (cutting) and generative or additive (joining) techniques. For the user it's only the result that counts. Therefore combined and even pure milling techniques are mentioned as well if the fit to the theme.

3. Application of Generative Processes on the Fabrication of Ceramic Parts

With respect to the use of generative processes in general it is quite surprising that all five generative processes mentioned above are available for ceramic processing as well, or, at least have passed the prove.

All processes that are suitable for ceramics, are based on ceramic powders. The powders are either pre-processed to a feedstock (ceramic foil or paste) or used directly.

Most of the processes first generate a green part which receives its final properties within subsequent follow up processes. The most common procedures are consolidation by sintering or reaction bonding (RB) using liquid silicon impregnation (RB-SIC). The main advantage of the latter is a negligible shrinkage.

3.1 Extrusion

Extrusion processes are close to conventional Ceramic Injection Molding (CIM). Basically all kinds of pasty feedstocks can be used that can be processed through nozzles with diameters smaller then 0,2mm. Generative machines that are designed for processing plastics can be used after modification of the extrusion unit and the nozzle.

The so called Multiphase Jet Solidification (MJS) process for the fabrication of ceramic parts by extrusion was developed already in 1994 at the IFAM in Bremen, Germany. The machine was originally designed as a test rig for low melting point metal powder-binder feedstocks in cooperation with the FhG-IPA, Stuttgart, Germany. A heated piston, filled with the feedstock applies the pasty material layer by layer. A couple of parts like the sample on **Figure 2** (left) made from silicon carbide have been processed.



Figure 2: MJS Part made from silicon carbide (SiC) made by IFAM, IPA, left. FDC Machine (middle), EFF Part (right).

After 1996 further impulses came from a US research program [ANL96] which concentrated on the fabrication of the feedstock. Most of the work was done on a modified generative machine

for plastic extrusion (FDM, Stratasys, **Figure 2**, middle). The so called Extrusion Freeform Fabrication (EFF) process is similar to the MJS-process but uses a rod-shaped feedstock. A high pressure extrusion unit was designed to deliver the necessary pressure for extrusion.

The closely related Fused Deposition of Ceramics (FDC) process is very close to the plastic process and works with the nearly unmodified machine. The feedstock therefore must be prefabricated as a mechanically stable filament. This makes both quite complicated, the fabrication of the feedstock as well as the generative process itself. Materials to be processed are Al_2O_3 (**Figure 2**, right), ZrO_2 und Si_3N_4 [VAI00].

3.2 3D-Printing

3D Printing is based on the powder - binder principle. Both are kept separately in the process. In the classical process, the binder does not contain ceramic particles and the powder does not contain binder. Recent developments show granules with different ingredients including binders and binders with nano particles.

The 3D Printing processes cover an extremely wide range of powder – binder combinations. The entire process is cold (room temperature) and does not use a laser. Therefore it is cheap and does not require a big effort for operation, infrastructure and maintenance.

As long as low viscosity binders are processed, industrial configured bubble jet print heads can be used. New binders based on polymers or waxes require adapted special print heads mostly of the piezo type.

The entire process is a two step one. First a green part is made by the generative process. It shows only approximately 50% of the theoretical density and a poor stability. Densification by isostatic pressuring is possible. The final density is achieved after de-binding, sintering and infiltration within suitable ovens.

A disadvantage is the fact that parts often show anisotropic properties which are caused by the low binding forces and the uneven wetting of the surface.

All 3D Printing processes of the powder-binder type which work with powder beds are based on a **MIT** patent (<u>www.mit.edu:8001/activities/tdp</u>).

Soligen (<u>www.soligen.com</u>) introduced its Direct Shell Production Casting (DSPC) already in 1993. DSPC is a process chain consisting of a machine and a CAD based shell design for precision casting applications. **Soligen** founded **Parts Now** which acts as a service bureau for castings. Therefore little is known about the materials and their properties.

Z-Corporation (<u>www.zcorp.com</u>) offers a variation of its basic process that uses a plaster based material and a water based binder. If it is used to make final parts, first a green part is made. To achive stability it needs infiltration mostly by wax or by epoxy. Another variation is the direct fabrication of shells for investment castings, called Z-Cast.

The 3D Printing process is very much suitable for making ceramic sculptures. The basic appearance is made by generative fabrication, the stability is achieved from infiltration and the surface quality such as texture, colour and shine result from manual treatment. The comparable high weight adds an intrinsic value to the sculptures so they are not regarded as fakes.

Marble powder was processed in a ProMetal 3D Printing machine by the IFAM, Bremen, Germany. The work was done in the context of the EU Project ECOMARBLE. (**Figure 3**, left). Possible surface effects due to manual post treatment are shown on the example of a tooth, **Figure 3** (right), that was made at the Rapid Prototyping Lab of the FH Aachen.

Based on the MIT patent, SpecificSurface (<u>www.specificsurface.com</u>) developed a proprietary process called CeraPrint. It is used to fabricate all kinds of products with defined interior structures, such as exhaust gas filters, water filters and heat exchangers. The company claims to process all materials which are listed in section 5 (below), even with additives to prevent corrosion. It delivers all kinds of custom defined geometries. The parts withstand thermo shock load and impulse cleaning (purging).



Figure 3: Sculpture, 3D Printing. Head of the Hygeia, Goddess of Health. Polished Marble Powder. (ProMetal, IFAM Bremen, left), Model of a tooth, Plaster-Ceramic (Z-Corp, RP Lab Aachen University of Applied Sciences, right)



Figure 4 : Water Filter Cartridge for a Coffee Maker, Diesel Exhaust Gas Filter Unit, Heat Exchanger Insert. Cera Print, SpecificSurface.

3D-Printing also is used to make resorbable artificial bone structures to be used as implants. A defined porosity supports the growing into the body and assures a rigid connection. Interior guiding channels allow an equal seeding of the cells and the growth of new bone material.



Figure 5: Demo Part with guiding Channels made from artificial Bone Material, 3D Printing (FORTEPRO, left), New Bone Material (blue/grey), grown in the guiding Channels (light grey/ white) of the new Bone Structure (blau/grey), (THERICS, right)

Comprehensive studies have been made in the research program FORTEPRO (<u>http://www.fortepro.de/</u>) of the Bavarian Research Foundation. Mainly hydroxyapatite (which is

a calcium phosphate) and tricalcium phosphate (also tri-calcium phosphate) were used to receive the required interconnecting porous bone structures needed (**Figure 5**). The US company Therics (<u>www.therics.com</u>,) commercialized a similar process (**Figure 5**).

Foundry Sands for metal castings are mostly mixed using binders on polymer basis which also can be processed with generative machines. The ProMetal process S15 (developed as Generis GS1500) applies the polymeric binder via nozzles on top of each sand. The resulting parts can be used directly in the foundry (**Figure 6**, left).

A variation of the classic 3D-Printing is called **Direct Ceramic Jet Printing** (DCJP, <u>www.ceram.com</u>). The binder contains ceramic particles. The process can either be run with or without an additional powder bed. The nozzle diameter is around 60 μ m and leads to droplet with an average diameter of 100 μ m. Smaller droplets lead to rich details of the part, but require an increased mechanical effort and finer nozzles which bear a greater risk of wear.

3.3 Sintering – Laser Sintering

The principle of laser sintering of plastic materials cannot be transferred directly to ceramic materials. While the low thermal conductivity of ceramics supports the process, the necessary high temperatures lead to a complex machine.

Foundry sand systems using polymeric binders open up a more easy solution. Already in 1992 the plastic laser sintering process was used to process foundry sand. Therefore the sand particles were coated with polymeric binder. The process was mostly used to make kernels which were equivalent to the ones made in the classic kernel making machines but showed a much more complex geometry. The results are similar to the ones received from the 3D printing process mentioned above This technology opened up new possibilities to the foundry people worldwide. As an example complex arrangements structures can be made. (**Figure 6**, middle and right).



Figure 6: Generative fabricated Kernels for Metal Casting. 3D-Printig (ProMetal, left) Laser Sintering (EOS, middle and right)

Sintering is also used to fabricate implants with porous hollow structures [WOE04]. Similar to the 3D printing the greatest problem is to clean these structures from loose powder.

The direct generative manufacturing of shells for investment casting by sintering was developed at the Fraunhofer IPT, Aachen (<u>www.ipt.fraunhofer.de</u>). The special feature is the very smooth surface. It has to be achieved within the process because it defines the surface quality of the latter cast part and it cannot be accessed for manual cleaning after the build.

To receive fully dense ceramic parts the powder must be melt completely. Such a system was developed by the French company **Phenix** (<u>www.phenix-systems.com</u>). The so called PM 250 (**Figure 7**) is designed as a high temperature laser sintering device with a fibre laser. It has a round build chamber with a diameter of 250mm and a height of 300mm and is heated to an operating temperature of 900°C. According to the company all ceramic powders (and even

metallic powders) can be processed. Ceramic powders must be sintered in a subsequent oven process.



Figure 7: Phenix Systems. Ceramic Part (left), Machine PM 250 (right)

Currently two developments on sintering processes underline the increasing importance of this process. Both processes originally had been optimized to process metals and will be adapted to ceramics. The micro sintering process developed by Regenfuß and Exner uses a proprietary micro sintering system which showed very interesting results. First results on ceramics are published in [REG05]. At the Forschungszentrum Karlsruhe Hansjosten adapted the Selective Laser Melting process to ceramics and succeeded to process first completely molten layers.

3.4 Layer-Laminate Processes

Laser based layer laminate processes (LLM) are basically suitable for making ceramic parts. The laser cuts all kinds of ceramic as easy as paper (if the parameters are set correctly).

The biggest problem is the joining of the layers. Fully dense parts are obtained after sintering of the whole stack. In this case the binder is only needed to guarantee the green stability. Many case studies show parts that had been made successfully using a partly manual doctor blade process (details see: [KLO99]). For industrial use a ceramic foil feeding mechanism has to be adapted to the basic paper lamination process. Its development finally led to the so called CamLem (www.camlem.com) process (the machine is named CL-100) which is commercialized by the homonymous company. According to the company materials to be processed are: Al_2O_3 , SiO_2 , ZrO_2 , SiC und Si_3N_4 (**Figure 8**).



Figure 8: CamLem Process. Machine CL-100 (left); Cylinder with integrated Cooling Channels (right).

LLM are suitable for making ceramic matrix composites (CMC) containing fibres or tissues, as long as they are prefabricated as flat woven fabrics or prepregs. Such a process which is additionally capable of processing parts with curved surfaces without stairstepping was described in [KLO99], (see: **Figure 9**). The special curvature is applied using a prefabricated gauge (that as well is made using paper LLM whose brand name is LOM) and thus enables the

process to make parts with a defined orientation of the fibres. In case of a flat LLM process the fibres would be cut at the border lines and the fibres would be damaged.

LLM processes are used for medical parts as well [GRI98]. In this case foils made from different materials are used, such as tricalcium phosphate and hydroxyapatite.



Figure 9: Layer Laminated Part. Flat LOM Process with Stairstepping (approx. 90 *90 * 18mm, left); spatial curved LLM Part (middle and right). All Parts are made from SiC [KLO99].

3.5 Stereolithography (sometimes written: Stereo Lithography)

The classic laser or lamp based stereolithography process is strictly limited to plastics. Ceramic parts can only be achieved by filling the polymers, which are needed to solidify the green part. Because a defined optical penetration depth is required for the process, the amount of filler material is limited.

Stereolithography resins filled with ceramic nano particles (ProtoTool resin family), a sort of composites, was introduced in 2004 by DSM-SOMOS. Although they were designed to allow higher loads and temperatures on plastic stereolithography parts, they show the way to ceramic parts. The recently (Nov. 2005) presented NanoForm 15120, which is a composite material filled with non-crystalline nano particles (www.dsm.com/en_US/html/dsms/home_dsmsomos) is about to continue this trend.

Paste Polymerisation. The basic idea of using the photosensitive polymer as a binder and carrier material for ceramic and metal powders was first introduced by the French company Optoform (which was acquired by 3D Systems in the meantime). Prefabricated pastes made from stereolithography resin and ceramic powders (35-60% fraction of ceramic material) had been layered on a build platform using a doctor blade mechanism. The solidification was done with a laser according to the contour of each layer. The process is a two step one. De-binding and sintering to a fully dense part is done in a subsequent oven process. Sample parts can bee seen on **Figure 10** (middle and right).



Figure 10: Stereolithography, Paste Polymerization. Machine (left), part and Turbine Blade made from Ceramics. (3D Systems-DSM Desotech /Optoform LLC)

Polyjet is called a procedure where liquid resins are processed through a multi-nozzle print head (Objet, <u>http://www.2objet.com</u>) directly on the build platform or on the semi built part. An instantaneous solidification is assured by a simultaneously operating high energy lamp. Seen from the material point of view the process must be called stereolithography while from the process perspective it can be looked at as a (3D) printing process too (see: **Table 2**). Until now there is only a small selection of only plastic materials such as standard, high loadable, coloured and elastic plastics. The introduction of filled materials is expected and will be the first step to ceramic and metallic materials and parts.

4. Layer Milling

As discussed above, more and more even layer milling is called a Rapid Process. This is correct if the milling is directly working with digital data. Based on a foil milling process, at the ETH (Zurich, Switzerland) a high precision layer milling process was developed [GAU02]. Some sample parts can be seen on **Figure 11** after sintering.



Figure 11: Layer Milling, ETH Zurich [GAU02]

In close cooperation with an industrial partner a high precision milling process for ceramic parts to be used in the restoration of teeth was created [N.N. Product Information DeguDe]. The process works with tetragonal polycrystalline zirconia.

5. Conclusion - Vision

As pointed out, all generative processes known today as Rapid Prototyping can be used to process ceramic materials.

The spectrum of materials used covers nearly the whole range of industrial ceramics: Parts and shells or cores are made from Al_2O_3 , SiO_2 , ZrO_2 and SiC. Fully dens parts are made from Si_3N_4 and so called graded materials are made from zirconium reinforced alumina (ZTA) by cladding ZrO_2 on top of an Al_2O_3 substrate.

Monolithic structures are made as well, but hollow parts with complex flow channels that can be loaded with high temperatures are in the focus. Defined macro structures are the basis for implants made from resorbable bio-ceramics. Micro porosity is used to create micro reactors but mainly to improve tribulogic systems.

The main advantage of generative processes is the possibility of realizing nearly unlimited geometries. Based on the tool-less fabrication future marketing strategies such as one-of-a-kind-production and mass customization can be realized.

As a precondition the range of materials must be increased and first of all, the surface quality must be drastically improved. As a fact, fabrication requires reproducibility and productivity but both of them are still weak points in the field of generative production.

As a perspective one can imagine material combinations and compositions which could never be realized with traditional fabrication technology. Not only composites can be made directly but so called designed materials that vary their properties through out each cross section of the part are no longer a fiction.

The Direct Ceramic Jet Printing (DCJP) for example covers the potential of making parts from different ceramic and non ceramic materials by applying it simultaneously from different nozzles. With this technology, functionally integrated parts, such as Micro Electronical and Mechanical Systems (MEMS) can be made directly from CAD data.

This is not just a vision but already reality. The Maskles Mesoscale Materials Deposition (M³D) is a process presented by the US company Optomec (<u>www.optomec.com</u>) that is suitable to make micro electronical parts. M³D is an aerosol printing process and works with a liquid colloidal solvent from different materials (**Figure 12**). The average droplet diameter is about 1 to 5µm. The materials to be processed must be at least smaller than 200µm diameter to be transported with the flow.

The process works with different materials, such as electronic inks, conductive polymers, isolating materials or biological components like proteins or cell suspensions and of course ceramics.



Figure 12: Maskles Mesoscale Materials (M³D) Process, Optomec. Process Scheme (left), Aerosol Printing Head (middle), Machine (right).

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