https://doi.org/10.2352/ISSN.2169-4451.2017.32.374

3D Printed Ceramics: Current Challenges and Future Potential

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Abstract

Materials and processes for additive layer manufacture have advanced considerably in the last few years and have moved the application of the technology away from prototyping to fabrication and manufacture. One area that still has little effective presence is that of 3D printed ceramics. Ceramic materials have proved difficult to integrate with 3D printing technologies and there is still a considerable way to go before the characteristics of most of these materials can be considered adequate.

The problems experienced are high firing contractions, low density and strength and potential incompatibility with glazes. For general tableware and giftware ceramics giftware ceramics two main methods of 3D printing are used, paste extrusion through a syringe and fine nozzle and a powder binder system that ink jets binder onto a powder bed containing a mix of ceramic powder and an organic binder.

The paste extrusion system has the advantage that conventional ceramic pastes and bodies can be used but the layer thickness is coarse and there can be problems with maintaining an even extrusion of a thin bead, the main issue with this method however is the restriction on geometric freedom that cannot compete with other 3D printing methods.

The powder/binder process gives the ability to form complex shapes, but has an inherent high porosity due to the burn out of organic binders and the restriction on particle size range required for the process to function correctly. The manufacture of high performance monolithic ceramics such as alumina and zirconia is achieved by using photo cure resins with a high loading of ceramic material, this requires a thermal de-bonding process that results in a very high firing shrinkage that can affect the dimensional stability in the firing/sintering.

The reasons for wanting to use ceramic materials are to utilise their unique properties but the limitations of the available processes make these properties difficult to realise by current additive manufacturing methods.

This paper will review and compare contemporary ceramic additive manufacturing processes and explain why the above issues exist and what potential solutions may be available. 2 The Centre for Fine Print Research at the University of the West of England in Bristol has a history of over eight years research into 3D printed ceramics and has developed and patented materials and processes in this area, and has collaborated with leading ceramic manufacturers and material suppliers in the U.K. to improve and refine the process.

Our ongoing research into this area is exploring potential solutions to these issues including hybrid extrusion/machining for paste extrusion ceramics, colloidal infiltration of preformed powder/binder 3D printed and novel methods of pre-processing the ceramic powders used in powder/binder 3D printing to increase the density and fired performance of the ceramic material.

Introduction:

Initially called rapid prototyping and used as method for generating short term prototypes this technology has been now known as 3D printing, and has advanced with the development of new processes and many improvements in materials and materials processing. These new technologies are increasingly being used to manufacture objects for end use and finished components

The material and process developments that have allowed this to occur in other field have not been so apparent in the area of ceramic materials, although new materials and processing techniques are on the horizon. This paper will discuss the pros and cons of the existing processes and materials, investigate new developments and try to indicate a possible path that ceramic additive layer manufacture may follow. [1]

What are Ceramics?

Pottery is often referred to as the oldest industrial process, with artefacts dating back to as early as 24000 BC having been found. Clay based ceramics have been refined and developed over the centuries to provide a sophisticated range of materials and processes that provide the art wares, domestic wares and building products that we enjoy today.

Technical and engineering ceramics arrive later in the timeline, these tend to be monolithic materials that require expensive processing and a very high sintering temperature are used in many areas and industries for their unique and desirable properties such as high temperature resistance, abrasion resistance and toughness. Examples include alumina, zirconia, silicon nitride, silicon carbide and bio-ceramics such as hydroxyapatite.

Advantages of 3D printing for ceramic materials:

1. The ability to form an object directly from a 3D file without the use of expensive moulds, dies and tooling.

2. The geometric freedom that 3D printing allows can have beneficial effects, it can be used for tableware art/craft ceramics and whitewalls to remove the design constraints inherent in conventional processing and to enhance aesthetic and practical aspects of the design.

For technical and engineering ceramics this design freedom can be used to enhance the efficiency and technical performance, an example is the 3D printing of ceramic catalyst materials to give a higher surface to volume ratio, the ability to form complex shapes in these materials can give a distinct advantages in use.

3. The ability to control porosity and to generate functionally graded materials.

Disadvantages inherent in 3D printed ceramic materials:

1. Some 3D printing platforms have restrictions on particle size of the powders that can be used in the printing process, the spreading mechanism in certain powder binder printers can have difficulty in cleanly spreading particles of significantly less than 50 microns, for certain ceramic bodies this can be a problem as particle sizes of around 5 microns would be optimal. This issue can have detrimental effects on the green strength and the fired strength, density and porosity.

2. Organic binders used in powder binder 3D printing materials need to be burned out (thermal de-bonding) in the firing (sintering) process, this again can be the cause of higher than optimal porosity and reduced density.

3. High firing shrinkages again caused by the organic binders and added to by the natural firing shrinkage of certain ceramic minerals can cause excessive distortion during the firing/sintering process and asymmetric shrinkage can add to a lack of dimensional accuracy.

3D printing ceramic processes:

Powder Binder 3D printing:

The first 3D printing process using ceramic materials was the powder binder process originally developed at MIT [2] this utilised essentially monolithic engineering type ceramic materials, it demonstrated the viability of 3D printing for ceramic materials and led to the formation of companies to exploit the technology such as Z Corporation and Specific Surface Corporation.

3D printed ceramics were further developed and commercialised by Viridis 3D, specifically for 3D printing alumina based metal casting moulds, although Figulo a company spun off from Viridis 3D extended the use of the material into ceramic artwork and giftware.

3D printable ceramic materials for the Z Corporation machine platforms have been developed separately by Tethon 3D and the Centre for Fine Print Research team at the University of the West of England[3] who have available a Tri-axial porcelain 3D printing material that replicates the characteristics of conventional porcelain. Allowing both conventional designs to be produced and giving the opportunity for previously impossible to make concepts to be realised.

Figure 1. *3D printed ceramic double walled beakers produced at UWE*

Along with the previously detailed issues with powder binder 3D printed ceramics with regards to porosity and density and strength, there is the question of scale and available platforms, the legacy Z Corporation platforms are no longer supported by the manufacture and spares and components will soon begin to dry up, these platforms also have a limited build volume which can be restrictive for certain applications particularly tableware, whiteware and architectural ceramics, for this area to develop a larger more reliable build platform is needed.

The Viridis 3D RAM123 system, developed for the rapid printing of metal casting moulds is capable of printing the large volumes required and has the potential to fulfil the needs of this sector but will require improvements in resolution and print quality to achieve this.

Fig2. *Viridis 3D RAM large format powder printer*

Extrusion Processes:

Since the advent of low cost self build 3D printers such as the Rep Rap project in the mid 2000's many researchers have explored paste extrusion systems to 3D print ceramic materials. Driven originally by the open source community several different types of extrusion heads have been developed ranging from compressed air driven syringes to motor driven auger systems and moineau pumps or even a combination of the two. In the UK this approach was pioneered by the artist/potter Jonathan Keep.
In Belgium Unfold-fab were an originator and have continued to develop and improve both the extrusion system and the 3D printer. Other exponents of these systems are Vormvrig from the Netherlands with their Lutum range of paste extruders and WASP from Italy who produce a range of Delta 3D printers.

WASP have scaled the concept up to a four metre high printer that is capable of printing large architectural structures for both ceramic and concrete.

Fig 3 *WASP large scale extrusion printer*

The main advantage with all of these paste extrusion printers is that they can use conventional ceramic materials. Decades of development into ceramic bodies means that conventional ceramic materials have been honed in terms of performance and behaviour.

The disadvantage with paste extrusion 3D printing is that the build layer thickness is very coarse compared to other 3D printing processes giving a distinctive layered appearance. It can be very difficult to extrude ceramic pastes through finer nozzles and if this was achievable there would be a corresponding unwelcome increase in build times. Geometric freedom and resolution is considerably reduced compared to powder/binder and resin/powder based 3D printing processes and fine detail and smooth surfaces are almost impossible to achieve. Extrusion processes possibly have a greater relevance to larger scale 3d printing of ceramics where these requirements are not as essential.

Photopolymer/ceramic powder processes:

A third way to form 3D printed ceramics is a photopolymer/ceramic powder system. In this process a photo cure resin is heavily loaded with a ceramic powder (usually a technical/engineering ceramic) and exposed to a laser or high intensity light. Iterative layers are laid down and cured to form a ceramic object. After curing, a thermal de-binding and sintering procedure is used to produce the finished ceramic and further post -processing may be needed.

An early proponent of this process was Cerampilot from France who developed a system using SLA technology to build objects in alumina and zirconia, Cerampilot was renamed 3D Ceram in 2010 and now has a 3D printed ceramic platform that can produce items for engineering ceramic uses, jewellery and biomedical applications.

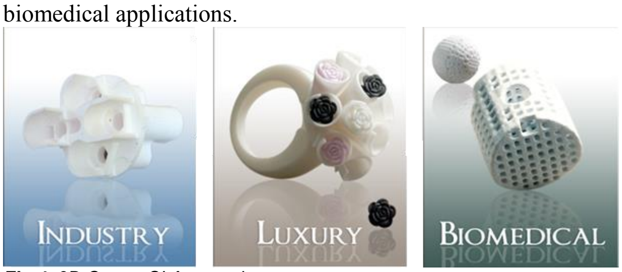

Fig 4. *3D Ceram SLA ceramic*

Lithoz, a company based in Vienna Austria using technology developed at Vienna University of Technology has a process that selectively cures ceramic loaded photopolymer resin with LED light to form objects in alumina , zirconia and Tri-calcium phosphate bone substitute.

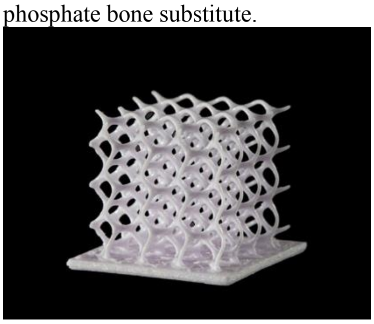

Figure 5. *Lithoz 3D printed ceramic*

Admatec is a Dutch company that has announced the release of a 3D printed ceramic system later this year. This again is a photopolymer/ceramic powder system using engineering/technical ceramic materials.

Photopolymer 3D ceramic printing systems have until recently been only available as high cost industrial level systems but early in 2016Tethon 3D from Omaha Nebraska announced the introduction of Porcelite ceramic resin suitable for SLA and DLP 3D printers. This material can be used in the less expensive 3D printers such as the Form 2 and Ember. This is an interesting development that brings the possibility of a low cost system for this technology but no information is available yet as to the composition of this material.

While a high density, high strength, high resolution fully sintered ceramic can be achieved all of these photopolymer ceramic systems have potential issues that can take a lot of effort to resolve. After printing and curing there needs to be a thermal de-bonding process to slowly burn out the polymer binder to allow the high temperature sintering process to take place to form the ceramic. This can cause a high shrinkage so that fine control over the firing regime is essential to minimise distortion. It can be difficult to achieve high loadings of ceramic material into a photopolymer resin.

The fact that these processes and the equipment involved can be very expensive means that they are best suited to technical and engineering ceramics where the requirements of resolution, sintered density and performance of the 3D printed ceramic can justify the costs involved.

Other 3D printed ceramic processes:

Shapeways:

Shapeways have developed their own 3D printed ceramic process, unusually it uses 3D printed moulds to allow the use of conventional porcelain casting slip. This gives a product that is easier to glaze than many other 3D printed ceramics and retains the properties and characteristics of conventionally formed ceramics, it does not allow the degree of design and geometric freedom as powder/binder and photopolymer/powder methods.

Robot-Hybrid Systems:

Extrusion based ceramic 3D printers have the advantage of using conventional ceramic materials with known properties and characteristics, but disadvantages in terms of geometric freedom.

Hybrid 3D printing using both additive and subtractive technologies, i.e. 3D printing and CNC machining is being used successfully for metal processing and there is the potential to adapt these methods for ceramic manufacture. The Centre for Fine Print Research at the University of the West of England is just beginning to research the possibilities in this area and to investigate the potential applications

HRL Laboratories LLC:

HRL Laboratories LLC have recently announced an interesting new 3D printing process to form a ceramic by printing a pre-ceramic monomer resin using an SLA stereolithographic printer.[4]

The ensuing polymer structure can be pyrolyses at a relatively low temperature of 1100 degrees Celsius to a silicon oxycarbide ceramic producing a material with a high strength, high density and corrosion resistance that is stable at 1700 degrees Celsius.

***Fig 6.** HRL Laboratories silicon oxycarbide ceramic*

HP:

HP announced this year their new HP Jet Fusion 3D printing system which promises to revolutionise powder 3D printing. Initially printing nylon powder materials there is great potential to print a much wider range of materials and strong and dense ceramics have been demonstrated.

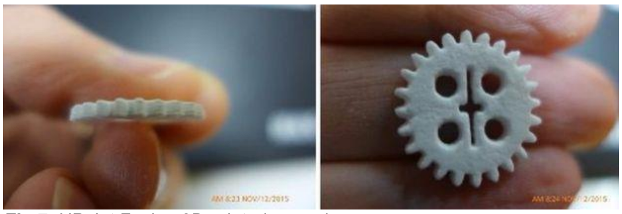

***Fig 7**. HP Jet Fusion 3D printed ceramic*

Summary:

Combining the unique and desirable properties of ceramics with the potential of 3D printing has proved difficult to achieve and much more work needs to be done to find optimal solution. Of the currently available processes the extrusion systems are showing advantages both for large scale architectural and sculptural ceramic and for low cost art/craft and educational applications.

Powder/binder systems have the advantage for tableware applications for product prototyping and design and geometry enhancement, current advances in equipment means that the issue with the scale and size of the final product are on the way to being solved. The issues of density and strength can be address by future improvements in material pre-processing and binder and inkjet technology advances.

The photopolymer/ceramic binder processes have the advantage in forming technical/engineering ceramic and future improvements in this area should give production rate and build scale improvements.

Intriguing developments such as the ceramic pre-cursor method demonstrated by HRL Laboratories and the new powder/binder technologies demonstrated by the HP Jet Fusion machine may be another step towards the final goal of 3D printed ceramics possessing both geometric freedom and the performance and characteristics of conventionally formed ceramics.

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Author Biography

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Having worked for over 25 years in the U.K. ceramic industry, he is currently researching 3D printed ceramics, photo ceramics and the use of digital fabrication techniques for Art/Crafts, Designer/Maker ceramics and industrial applications. In 2011he was awarded the Saxby medal by the Royal Photographic Society for his work on 3D imaging.