A review of process development steps for new material systems in three dimensional printing (3DP)

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ABSTRACT

Three dimensional printing (3DP) is a method for direct digital manufacturing that provides capabilities for creating a wide range of part geometries (including internal channels) in a broad variety of materials, including just about anything that is available as a spreadable powder. Taking advantage of the full variety of materials requires development of specific implementations of 3DP. This paper organizes the process of 3DP implementation into five steps (powder formulation, binder method selection, binder formulation and testing, printing process specification, and post-processing specification) and presents a review of the literature relevant to each step in 3DP implementation.

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1. Introduction

This paper presents a review of the literature related to the development of new material systems for three dimensional printing (3DP). A 3D printer is a tool for direct digital fabrication that selectively prints a liquid binder into a bed of loose powder to form a green part whose shape is given by CAD specifications [1]. Successful realization of a specific 3DP process involves not only the printing process itself, but also the formulation of a suitable combination of a powder and binder material system along with process details for printing and post-processing, both of which play a major role in determining the mechanical properties of the

parts produced. While a significant strength of 3DP is the wide range of potentially suitable materials, including polymers [2–12]; metals [13–15]; and ceramics [1,16–24,14,25–30] (or anything else that is available as a depositable powder with particle size in a suitable range), creating a specific instantiation of 3DP with a new material combination requires a number of steps: (1) formulation of a powder, (2) selection of a binding method, (3) formulation of the liquid binder and testing its suitability for printing and interaction with the powder, (4) specification of printing process parameters, and (5) specification of post-processing procedures.

This review presents a summary of information relevant to each of the steps in the development of a new material system for 3DP. Section 2 covers the literature on powder formulation, Section 3 provides detail on the different available binding methodologies, Section 4 discusses liquid formulation, Section 5 explores the powder–binder interaction and part printing, and Section 6 covers post-processing options. The material presented is drawn from searches of databases of both research publications and issued patents, along with a few conclusions from the authors' own experience. The authors note that, perhaps due to the early commercialization of 3DP, 34 of the 81 citations refer to patents, compared to 47 from other technical publications.

Several companies produce machines for 3DP, but there is a relatively small number of commercial material systems. Voxeljet Technology (Augsburg, Germany) has a sand-based system for metal casting and a PMMA-based system for plastic parts. Z-Corporation (Burlington, MA) also has a sand-based system for metal casting as well as systems for composite or elastomeric parts. ProMetal, a division of ExOne (Irwin, PA), has a sand-based metal casting system as well as metal-based material systems, including stainless steel, bronze, and high noble gold. The lack of readily available material systems is a motivating factor for the creation of new material systems when one of the currently available material systems is not appropriate for the intended usage.

1.1. Advantages of 3DP

With a resolution similar to or better than most of the rapid prototyping (RP) systems, 3DP also offers a unique opportunity to take advantage of previous work in other fields and adapt it successfully. When adapting a powder-based process, the pre and post processing may remain similar, but 3DP can be used create shapes that are difficult or impossible to create by traditional means. The thermal post-processing steps for ceramics and metals are similar to those in traditional powder-based methods and do not require the potentially extensive laser optimization experimentation of selective laser sintering (SLS) [31] and selective laser melting (SLM) [32]. The drawback of 3DP is that parts require post processing and typically have considerable porosity (even after initial thermal treatment), while SLS and SLM parts come out of the machine fully dense (SLM) or already sintered (SLS) and ready for infiltration [33]. The polymer field does not have the same 3DP parallels as metals and ceramics (because processing in a powder state is less common), but tissue engineering in particular has steps that are adaptable to 3DP because scaffold fabrication often begins with microspheres of the correct sizes for 3DP [34]. In addition to the fabrication flexibility of 3DP, these adaptive abilities of 3DP make it a powerful tool as a modifier to a traditional fabrication process, as opposed to the complete process reinvention required when using new materials in other RP systems.

2. Powder selection

The powder formulation process includes material selection, particle sizing, additive selection, and deposition optimization. Powder formulation is generally the first step in 3DP because in most cases the powder material will make up the major volume fraction of the final part. After printing, a typical green body (the printed part before post processing) can be 30%–75% vol powder, 10% vol binder, and the rest void space [13]. A benefit of 3DP is that there are no limitations on the material selection as long as it can be formulated into a powder suitable for the selected deposition method.

2.1. Powder formulation

The most important powder property is depositability, which depends on the size and shape of the particles. Deposition can be performed with the powder in either a dry or wet state, but the acceptable particle sizes are different for each deposition process. Particles that are 20 microns and larger are preferably deposited in the dry state, while particles smaller than 5 microns can be deposited in either the dry or wet state [35]. Fine powders (∼1 micron) tend to agglomerate due to van der Waal's forces and moisture effects [36], so mechanical spreading can be problematic. Fine powders can be deposited in a dry state, but only as a low volume percentage in a predominantly larger diameter powder formulation or as bound agglomerations of smaller particles [37]. Fine particles can instead be deposited as a slurry when the particle size is less than about 5 microns [35]. In both dry and wet deposition methods, the particle shape is less important than the size, but spherical powders are preferred for dry deposition because they tend to flow better [2] and have low internal friction [37]. Faceted or anisotropic powders have much more frequent interparticle contact than spherical powders, and the increased internal friction lowers the spreadability of powders with these particle shapes, but may increase the packing ratio [37].

The particle size affects design parameters of both the printing process and the final part. A summary of how the powder characteristics affect the printing process is shown in Table 1. Part parameters affected include sinterability, pore size, surface area, surface roughness, and minimum feature size. Fine powders have the potential advantages of increased sinterability, lower surface roughness, smaller minimum features, and thinner layers [36]. Larger particles are easier to spread, have lower surface area per volume [38], and the larger pores facilitate fluid migration through the bed to aid in the production of more homogeneous parts [39].

Multimodal powder formulations containing a variety of particle diameters can offer the benefits of both small and large particle sizes. The large particles allow the powder mixture to be spread in a dry state, while the smaller particles fill the interstices between the large particles to increase the bed density [43] and offer the aforementioned smaller particle size benefits. The potential density increase can be particularly significant; for example, the tapped green density of a coarse bronze powder increases from 59.3% to 73.2% with the addition of 31% vol fine copper particles [43]. More information on powder characteristics and selection can be found in associated powder metallurgy references [44].

Additives can be added to the bulk material to affect the powder depositability, printing behavior, final part properties, and post-processing behavior. Dry powder deposition can benefit from a solid lubricant in low weight percentages (1%–2% wt) [26] or by surface coating the powder to reduce internal friction [45]. The printing behavior of a powder can be affected by adding a material like lecithin that causes light adhesion between particles and inhibits powder aerosolization and the resulting part

Table 1
Powder characteristics and the influence on deposition, printing, and post processing.

	Advantages	Disadvantages
Size		
Large particles >20 μm	Can be spread dry [35], lower surface area per volume [38], large pores facilitate fluid migration in bed [39]	Largest particle establishes minimum layer thickness [40]
Small particles <5 μm	Increased sinterability, lower surface roughness, thinner layers, smaller minimum features [36]	Difficult to spread, agglomerate due to van der Waal's and moisture effects [36], higher chance of ballistic ejection during droplet impact [41], may require slurry deposition [42]
Shape		
Spherical	Tend to flow well [2], low internal friction [37]	
Faceted/Anisotropic	Potentially increased packing ratio [37]	Higher internal friction inhibits spreading [37]

distortions [46]. To affect the part properties, longer fibers (no greater than the layer thickness) can be added to the powder to reinforce the final part, while shorter fibers (no greater than half of the layer thickness) can increase the dimensional stability [46]. The fiber additions can be polymers, ceramics, graphite, fiberglass, etc. [39]. There is an upper limit to fiber loading because the fibers reduce the packing density of the bed and make spreading more difficult due to increased internal friction [39]. Additives to affect post processing include oxygen scavengers to reduce the oxide layers on metal powders [47] and sintering aids [48]. Regardless of function, any potential additive should mix uniformly with the bulk powder so as not to create uncontrolled inhomogeneity in the final part.

2.2. Deposition methods

The deposition method might be selected concurrently with the powder formulation selection but is usually fixed by the 3DP machine. Both dry and wet application of powder have unique characteristics, but in both cases the goal of layer spreading is to deposit smooth and uniform thickness layers with a minimal layer formation time [49]. Dry deposition is preferred due to the simplicity, ease of testing, and speed [1]. For dry deposition, the preferred particle diameter is greater than 20 microns [35], with example size ranges of 15–30 microns [41], 10–50 microns [40], and 45–60 microns [43]. Each spread layer is preferably at least three particles thick due to issues of powder flow and spreadability [36] and should be thicker than the largest particle [40]. A common method of dry powder deposition is a traversing counter-rotating roller (the roller direction at the bed surface opposes the traverse direction) that can deposit new layers of material without disturbing the previous layers [46] and serves to push the new powder in front of the roller as it traverses to assist in the powder distribution [50]. The roller can also be charged [49] or vibrated [51] to facilitate spreading. Other dry application methods include fluidized beds [52], traversing doctor blades [37] that can be vibrated to aid in powder flow [42], rotating sieve drums [37], and charged plates [53].

The alternative to dry powder deposition is to deposit fine particles as part of a slurry. The slurry is deposited onto the surface of the powder bed, the liquid carrier is removed via slip casting and drying, and the solid material is left behind [36]. Due to the capillary effects of the drying liquid, the density of the deposited layer is higher than that of dry deposition, but the process drawbacks include longer layer deposition times [1] and potential layer cracking [36]. The solids loading of a slurry can be as high as 65% vol [42] and they form layers as thin as 10 microns that are more than 50% dense [36]. After printing, the entire slurry-deposited bed can be immersed in water to disperse the excess powder that is surrounding the printed part [22]. Slurry-specific additives include dispersants to reduce the viscosity of slurries with high solids loading [42] and redispersing agents to

help separate the loose powder from the printed part if the powder bed is submerged after printing [36]. Layer cracking during drying may be avoided or minimized by increasing the solid volume fraction of the slurry, decreasing the carrier fluid surface tension, increasing the fracture resistance of the film, increasing the contact angle between the slurry and the solid, and increasing the pore radius of the film [36].

Because the bed density has a direct effect on the density of the green part, increasing the packing density of each deposited layer is often desirable. Dry powders can be compacted using mechanical vibration, acoustic energy, sonic/ultrasonic vibrations, or a piezoelectric scraper [35]. Compaction can also be achieved purely mechanically by spreading a layer with a counter-rotating roller, raising the build chamber, and rolling over the bed a second time with the roller spin corresponding to the traverse direction [37]. The bed may be densified by wetting the top surface of the powder bed and allowing capillary action to repack the particles. Volatile liquids are preferred for this application because they evaporate quickly and tend not to accumulate, but liquids designed to leave small amounts of residue that add to the cohesive strength of the bed are also potentially useful [37].

In addition to the 3DP-based literature, more information on powder deposition can be found by examining the appropriate SLS literature because, like 3DP, SLS begins with the deposition of a thin layer of powder. Associated references include investigation of ambient gas pressure on powder flow [54], examination of layer quality as a function of deposition method [55], and aerosol spray deposition of alumina powder beds [56]. More general information on powder flow properties and various dispensing techniques can be found in a 2007 *Powder Technology* review paper [57].

3. Binder selection

After formulating a powder, the next step is to select the binding method and formulate the liquid. There are a number of different ways of binding the powder, but some of the common selection criteria include binder location (in-liquid vs. in-bed), binder residue in the final part, and binder material limitations.

3.1. Selection criteria

The location of the binding agent has an effect on the versatility and reliability of the liquid. A liquid binder (for example, a suspended polyvinyl [26]) contains all of the binding components in the printed liquid and will often bind a large variety of powders, but liquid-only binders tend to have higher incidences of printhead nozzle clogs than inert liquids [46]. An in-bed component of a binder system is mixed with the powder, and binding occurs where it interacts with the deposited liquid. An in-bed binder such as plaster may allow use of a more reliable liquid [39] but requires an additional powder formulation step any time a new powder is selected.

Another of the common binder selection criteria concerns the binder residue and how it affects the strength and purity of the final part. A fugitive binder leaves little or no residue after processing but requires that the powder particles be bound by a secondary process after printing because the binder does not contribute to the final part strength. An example fugitive binder is chloroform, which acts to bind some biodegradable polyesters and evaporates in the process [7]. Other binders can leave a residue that contributes either partially or fully to the final strength of the part. For example, inorganic binders can deposit structural materials (such as aluminum nitrate [25] and silver [14]) that contribute to the part strength [37]. In the extreme case, bulk powders such as plasters and cements are self-binding (and require no added binding agent) because hydration activates the material and leads to a setting reaction [58,40,59].

The last of the binder selection criteria relates to potential material limitations. These limitations are generally a result of the binder thermal processing. If a binder requires heat to reach full binding strength, then the powder is limited to a material with a phase-transition temperature higher than that of the binder to avoid altering the part during heating (for example, colloidal silica must be fired to convert to pure silica [60]).

3.2. Binding options

The following section is a review of various 3DP binding methodologies. The basic traits and common examples of nine different binding methods are discussed. The methods presented are: organic liquids, in-bed adhesives, hydration systems, acid/base systems, inorganics, metal salts, solvents, phase-changing materials, and sintering aids/inhibitors.

An organic liquid binder is one of the most versatile binder methodologies. Organic binders have the benefit of working with almost any powder material and can thermally decompose to leave little residue. Possible organic binders include butyral resins [1], polymeric resins [58], and various polyvinyls [26]. The liquid reliability is a concern because clogging can occur if an organic-loaded liquid dries in the printhead [61], but this can be addressed during liquid rheological development. Most organics break down in the 200 °C–300 °C range [22], but carbohydrates have been shown to continue contributing to the part strength even when heated up to the sintering temperatures of some metals [13]. Another subset of organic binders is preceramic polymers such as polycarbosilazane [1], polysiloxanes [61], and aluminum amides [62]. These polymers behave as organic binders during printing but can be thermally reacted in specific gaseous environments to deposit ceramic materials.

An alternative to a binder-loaded liquid is an adhesive in the bed that binds the powder after interacting with the deposited liquid. Materials like maltodextrin [11] and sucrose [46] dissolve when the liquid penetrates the bed, spread in a localized area, and bind the powder as the volatile components of the liquid evaporate [46]. An adhesive in the powder allows the use of a simpler deposited liquid and can achieve a higher adhesive loading than is possible with a liquid binder [46]. In-bed adhesives should be highly soluble in the deposited liquid and have low viscosity when dissolved (to enhance pore filling), low hygroscopicity (to avoid moisture absorption from air), and high bonding strength [46]. The adhesive can be in particulate form in the spreadable range (10–40 microns) [40] or can be coated on the powder particles [39]. Like organic binders, in-bed adhesives are typically not material specific [2] and can be thermally degraded to leave little residue.

Hydration-based systems are another solely in-bed methodology that involves using a bulk material that binds itself when wetted. Like in-bed adhesives, hydration-based systems work with simple liquids so the printing reliability can be high. The common materials that exhibit hydration-activated binding behavior include plasters [58] and cements [40,59]. Both can be structural materials and have the added benefit of being well understood and reasonably inexpensive. The setting behavior of these materials can be altered by adding a catalyst to the powder to reduce the amount of water needed to initiate setting or to speed the setting process [58,59].

Acid–base systems rely on the controlled interaction of two components to initiate binding and can be used to bind most materials [9]. An example system is acidic and basic electrolyte coatings of polyvinyl pyrrolidone on the powder particles that result in strong bonds when activated by water and leave little residue when thermally processed [9]. The acid–base reaction can be initiated by printing one component in liquid form into a powder containing the other component, depositing one component in each of two liquids, or placing both components in the bed and initiating the reaction with a solvent. Acid–base systems can also be combined with other binding systems. For example, the quick binding of an acid–base system will give initial strength to a plaster system that will then continue to gain strength over time as the plaster sets [40].

Inorganic binders are typically incorporated into the final part and are often silicate-based [37]. A common selection is colloidal silica due to its variety of uses and ease of manipulation. When a stabilized colloidal silica solution (pH 9–9.5) is printed into a powder bed containing an acid or is exposed to gaseous CO_2, the pH drops, the colloid gels, and the powder is bound together [60]. When fired, colloidal silica deposits silica that remains in the part and contributes to the part strength [1]. Another inorganic methodology involves depositing solid material into the bed by printing precursors or solid dispersions [5]. For example, aluminum nitrate decomposes to alumina and can be dissolved in deionized water [25]. Solids can be deposited directly in dispersions with oxides such as alumina, which can be surface treated to form stable aqueous suspensions that are printable [63]. The deposited solids may not act as a binder immediately after deposition, but the entire bed can be heated after printing to convert, melt, or sinter the deposited material to bind the part within the bed before depowdering.

Metal salts are binders that are particularly useful for metal powders because two of the three binding pathways result in metal being deposited into the powder bed. Mechanical binding occurs as the liquid dries and the salt recrystallizes. Recrystallization binding works with any powder material as long as it is not soluble in the salt solution [14]. The second binding pathway is to thermally reduce a crystallized salt to its base metal, which remains in the bed and joins the powder particles. The only additional constraint for salt reduction is that the bulk material must survive the reduction heat treatment [14]. The last binding pathway is a salt displacement reaction. Salt displacement is material specific and occurs when the bulk powder dissolves into the salt solution and metal from the salt deposits on the powder particles. The dissolved metal dries into a salt form and may be reduced back to metal with heat treatment [14]. Metal salts may be utilized as both in-liquid and in-bed binders. Example salts include silver nitrate, which reduces to silver at 440 °C, and a copper sulfate–tool steel powder combination that results in displacement-induced deposition of copper to bind the tool steel [14].

A nonbinder approach for polymer powders is to deposit a solvent into the bed. A solvent will dissolve part or nearly all of the particles it comes in contact with, and as the solvent evaporates the polymer reprecipitates to leave connected particles [5]. For example, chloroform has been used to bond biodegradable polyesters [7] and PLLGA–salt mixtures [6]. Multi-solvent solutions can be employed to balance the stronger binding of an aggressive

solvent and the reduced warpage risk of slower evaporating, low vapor pressure solvents [2]. Solvents are particularly useful when part purity is a concern because solvents evaporate and potentially leave little or no residue in the final part.

Phase-changing materials as binders work with most powders but limit the potential post-processing temperatures of the printed part. If a room-temperature solid with a low melting point is deposited into a heated bed, the material melts and penetrates the powder on contact [37]. The material solidifies when the bed is returned to room temperature and the powder is bound together. Another variation is to deposit a lower melting temperature material like 2-methylpropane-2-OL in a liquid state using a heated printhead so that solidification occurs upon contact with the powder bed [37]. In both cases, because the original binder can melt, there is a limit on post-printing heating of the part if no secondary binding or infiltration is performed.

Another method of achieving binding is to locally affect the thermal behavior of the powder to control sintering by depositing different materials. For example, induction heating of a powder bed with selectively deposited metal flakes results in non-uniform melting behavior of the powder and can result in selectively bound regions within the bed [53]. A related approach involves the deposition of an inhibitor in select areas of the bed and layer-by-layer or bulk binding and/or sintering of the entire bed. Selective inhibition can include the deposition of heat-reflective materials, heat-isolating materials, sintering inhibitors, and chemical oxidizers [64]. Sintering inhibition has the potential benefit of only requiring deposition at the part boundaries, but has the drawback that in most cases the entire bed will be affected by processing and the excess powder will be either sintered or contaminated [64].

More information on binder selection and individual binder options can be found in related literature in other powder-based fields. Some examples include sand casting [65], injection molding [66], and microcasting [67].

4. Liquid formulation

The next step after selecting the binder methodology is to formulate the printing liquid. Even if the liquid itself does not carry a binder component, a liquid must be printed into the bed to initiate the powder binding process. As a result, any new 3DP materials system requires a liquid formulation step.

The most important liquid characteristic is reliable deposition. A liquid that binds flawlessly but only deposits sporadically is of little use in producing the desired part. Regardless of the exact binding method, to function effectively a deposited liquid needs to be able to penetrate the top layer of powder and sufficiently wet the next layer to ensure adhesion between layers [59]. Rapid binding is preferred to increase the rate at which new layers can be deposited [68] because a binder that is not fully hardened can affect the deposition of the next layer [1]. Prior to printing, a liquid should be stable, easy to rehydrate, and slow to dry. After printing, the stability requirements reverse [60].

The selected binding methodology establishes the foundation for the liquid development. In addition to any binder components, the deposited liquid may contain additives to aid the printing process or to affect the final part. The liquid may include "water, surfactants, organic solvents and co-solvents, buffers, biocides, sequestering agent, viscosity modifiers, low molecular weight polymers, lithium ions sources, etc." [59]. Other printing aids may include humectants to help reduce nozzle clogging [60], a pH indicator [60], flowrate enhancer to increase deposition rate [46], dye [40], and thickening agents to arrest droplet spreading [36]. The combination of the carrier fluid, potential binding agents, and additives determines the rheology of the final liquid formulation.

4.1. Liquid rheology

The liquid reliability is dependent on the rheology and proper matching of the liquid characteristics to the printhead specifications. Printheads typically have an optimal and an extreme range for both surface tension and viscosity as well as an upper limit on suspended particle size. Most commercial inkjet print-engine manufacturers specify a maximum fluid viscosity of about 20 cPs [69], but printers can be designed to handle up to 100 cPs [61]. The minimum acceptable surface tension is about 35 dynes/cm [61]. In theory, the maximum particle size is only slightly smaller than the smallest channel in the printhead, but this significantly increases the chances of clogging and increases wear on the head [70]. A useful rule of thumb for reliable deposition suggests a suspended particle size at least 100 times smaller than the nozzle diameter [15].

Surface tension is the easiest rheological property to alter, and it is most commonly changed by adding a fluid with a different surface tension [36]. While water is a common carrier fluid, a surface tension of 72 dynes/cm exceeds the specified value for many printheads. The surface tension of a water-based liquid can be reduced (by ~35%) with the addition of a lower surface tension fluid such as methanol in small quantities (20% vol) [18]. While surfactants are frequently employed to alter surface tension in other applications, the mechanics of how surfactants lower surface tension can make them ineffective for 3DP. Extra surfactant in a solution groups together into micelles and as new liquid surfaces are exposed the surfactant migrates to these surfaces and acts to lower the surface tension. This is problematic for 3DP because the migration of the surfactant to the newly created liquid surfaces is not necessarily able to match the speed at which the drop surfaces can be created. Subsequently, the surface tension experienced by the printhead may be similar to that of the bulk fluid without the added surfactant.

The viscosity of a liquid is more complicated than surface tension and is affected by factors including pH, solids loading, polymer loading, and polymer length. If the solution is particle loaded, the viscosity can be reduced by lowering the solids loading [61] or adding dispersant [42,19,71,72]. The viscosity can also be decreased by increasing the mean particle size while maintaining a fixed solid loading, but this option is of potentially limited use given the increased printhead wear and higher risk of nozzle clogging associated with larger particles [70]. For a polymer-loaded solution, the viscosity can be lowered by shortening the polymer chain [70,59] or lowering the polymer loading [22]. More universal approaches to altering the viscosity that can affect both particle-loaded and unloaded solutions include changing the pH [16,19,41] and diluting the fluid.

4.2. Liquid behavioral characteristics

After tailoring the rheology, the liquid should be tested for rehydration and stability characteristics. The rehydration behavior is important because a liquid that is not easily self-soluble may have trouble dissolving clogs and decrease the reliability of the printhead. For a particle-loaded solution, it is of particular importance to not rely on suspension aids that evaporate because they will not contribute to supporting a redispersed solution [60]. Stability testing should include aging and subsequent testing of the liquid's pH, viscosity, and surface tension [60]. Stability is particularly important for suspensions because the viscosity can potentially change on time scales as short as a few days [63]. Stability can be tested by measuring the optical transmission through a liquid sample [60] and looking for premature polymerization and/or coagulation that are signs of an unstable binder. A suggested final step before printing is to filter

the binder to eliminate agglomerations of liquid components that might otherwise inhibit the printability [73].

A liquid that is in the correct rheological ranges for the printhead and has adequate rehydration and stability characteristics is suitable for test printing. Print testing may include examination of customized droplet generation, drop volume versus drop frequency, and droplet trajectory as a function of droplet velocity and carriage motion [74]. These techniques are not 3DP specific, but the process development for a 3DP liquid is the same as that for a traditional inkjet fluid. The development strategies for traditional inkjet fluids can include printing quality and reliability tables useful for troubleshooting as well as documented rheological reformulation strategies [74].

5. Powder–binder interaction

After powder and liquid formulation, the next step is to examine how well the two work together. The liquid must be able to interact with and bind the powder to achieve a successful 3DP process. For example, a hydrophobic powder and a water-based liquid may not form an acceptable system even if individually they each meet the desired selection criteria.

5.1. Compatibility testing

Benchtop tests are powder–liquid interaction examinations that can be done outside of the 3DP machine. For example, a pile of the powder can be strafed with a syringe of the 3DP fluid and then examined after drying. Positive results include quick absorption of the liquid into the powder and cohesive 'pebbles' of bound material after liquid evaporation, but if no absorption or binding occurs then the powder–liquid combination may not be suitable for 3DP [58]. Another benchtop test involves manually mixing different powder:liquid ratios to provide data on the required binder loading for a desired green strength. These mixtures can be cast into bars and examined when dry. A good system should produce a dry part that retains edge definition, has enough green strength to be handled gently, and breaks cleanly as opposed to crumbling. Additionally, the bars can be post processed in the same method proposed for the printed parts to provide initial insight into the curing, sintering, and/or infiltration behavior of both the binder and the powder material [75].

5.2. Printing

There are two types of printheads for the generation of liquid drops. Drop-on-demand (DoD) printheads work by generating individual drops on demand. The two common DoD printheads are piezoelectric and thermal inkjet heads. Piezoelectric heads work by squeezing out ink drops as the shape of a small chamber is changed piezoelectrically [74]. Piezoelectric heads can ease ink development because the only requirement is that the rheological properties of the ink must be such that the ejected ink forms a reliable droplet. Thermal inkjet heads work by vaporizing the liquid in the printhead and using the subsequent volume expansion to eject the ink from the printhead [74]. The important ink considerations for thermal inkjets is that the vaporized liquid redissolve quickly and the ink does not permanently deposit solid material in the printhead. Continuous-jet (CJ) printheads constantly generate liquid droplets and are able to print at higher rates than DoD printheads but require that the ink be inductively chargeable so the drops can be deflected into a gutter when not being deposited [74]. Continuous-jet printers offer the option of proportional deflection, slower traverse speed, and more control over overlapping primitives for a smoother part surface finish than DoD heads [17].

The goal of printing is to reliably deposit a liquid to the powder bed and selectively bind the powder. The liquid impacts the bed, spreads to the surrounding powder, and then rearranges and binds the powder [45]. The main impact-related concerns are ballistic erosion and ejection [36] and the subsequent trenching and powder redistribution [41]. The impact effects can be reduced by lowering the energy imparted into the bed by the droplet [45] or by increasing the cohesion of the bed [46]. The liquid spread characteristics are important because a liquid that wicks out considerably from the impact area results in a rougher surface texture [5]. The spreading can be directly retarded by increasing the liquid viscosity [2] or using in-bed components that increase the liquid viscosity as the components dissolve [46].

After the spreading and absorption of the deposited liquid, the fluid component is removed. After impacting the bed, the liquid behavior is described as follows: "Immediately upon printing it may completely or nearly completely fill the voids, but capillarity then draws some of the liquid off into surrounding powder until an equilibrium configuration is reached. In spherical powder, this equilibrium configuration may typically result in about 60% of the void volume being filled by liquid. At this stage, the liquid in the voids is connected" [14]. Evaporation causes the liquid to become disconnected as surface tension draws the liquid to the high-curvature regions at the contact points between powder particles. As the remaining liquid continues to evaporate, the liquid saturation level increases, and any material that is suspended in the liquid is deposited as a ring around the interparticle contact points. This localized deposition is desirable because the formation of strong parts requires that 6%–10% of the material in the finished part contributes to the connections between powder grains [60]. Printing highly saturated fluids requires special attention because, if the critical saturation level of the binder is reached too early, some material may not be deposited around the particle necks and will not contribute to the green strength of the part [14].

5.3. Feature generation

Printing systems can be characterized by examining the generation of features. In general, the feature size "is primarily dependent on the size of the binder droplets used, while the tolerance on such dimensions primarily depends on the degree of the reproducibility of the droplet spread characteristics of the binder material which is utilized" [37].

The basic building block of a 3DP part is a primitive. A primitive is the bound agglomeration of powder that results from the interaction between a single liquid drop and the powder bed [2]. A typical liquid is capable of binding particulates several times the mass and volume of the fluid droplet [58]. For example, an 80 micron diameter droplet of colloidal silica binds a 30 micron alumina powder into 120 micron diameter primitives [17].

Lines are formed by overlapping primitives. Line dimensions are a combination of the powder–liquid interaction and the printing parameters, but are generally of a thickness similar to the primitive diameter [5]. The line width increases with increasing jet velocity and more binder volume per length, and decreases with increasing viscosity, increasing wetting angle between liquid and surface (less effective wetting) [36], higher surface tension [22], increasing printhead velocities, and smaller particle sizes [2]. The theoretical relation between line diameter and drop spacing is given by $L = K(S)^{-1/2}$, where L is the line diameter, K is a constant depending on the combination of the liquid and powder bed, and S is the drop spacing [23]. A unique result of printing lines in bimodal powders is the preferential distribution of the fine particles on the surface of the line, which produces an enhanced surface finish. This smoothing is most effective when the drop spacing is small but

must be balanced with the subsequent higher binder dosage and increased line thickness [23].

To examine the useful capabilities of a system, test parts can be developed and printed to study the formation of planes, walls, channels, and other features. Arrays are particularly useful test parts because, for example, if only six out of ten elements of an array of decreasing thickness walls are successfully printed, the minimal wall thickness is immediately known within a fairly small range. Because the part orientation relative to the printhead travel path affects printing, the test parts should either be designed to examine this behavior, or the same test part should be printed at various orientations. Test parts can also be used to compare different powder–liquid combinations when multiple systems are being developed [76].

6. Post processing

The result of a successful 3DP material system after printing is a bound part embedded in a loose powder bed. While getting to this point represents a considerable portion of the required 3DP-specific knowledge, processing the part to a final state cannot be overlooked. The only required step remaining is the removal of the part from the powder bed and subsequent removal of excess powder, but other post-processing steps may include post-printing bed manipulation, sintering, and infiltration.

6.1. Post-printing bed manipulation

Prior to depowdering, some binder systems benefit from a bed manipulation step. A drying step is beneficial for most binder systems to eliminate excess liquid in the green part and ensure that all of the intended binding agent is contributing to green strength. Drying is particularly important for plaster and cement-based systems because additional strength can be obtained through forced drying [58]. A curing step can be used to increase the binding strength of some organic binders by furthering polymerization. Potential curing options include visible light, vacuum, heat, and pressure [28]. Other bed treatments might include reduction of a salt-based binder [14], conversion of a preceramic polymer [62], or sintering of an entire bed with selectively deposited sintering inhibitors [64]. The main limitation on any bed manipulation step is that the treatment should affect only the printed regions of the bed and not fuse, react, or otherwise solidify the entire powder bed with the part embedded within.

6.2. Depowdering

The next step after bed treatment is to remove the loose powder from the part. For a part with no internal features, this can be performed manually by brushing or gently blowing away the excess powder. For slurry-deposited parts, the entire bed may need to be deposited in a solvent to break up the unbound particles [36]. Complex or internal features can be more difficult to completely depowder and may require additional steps. Dry options include blowing air, vacuuming, and vibration [77]. Adding smaller particles prior to vibration helps to remove loose particles and improve the surface finish. Part contamination can be avoided by vibrating with sacrificial materials like salt or particles of the same material as the part [16]. Wet depowdering is an option as long as the binder is not soluble in the fluid. Wet options include ultrasonicating [5], microwave-induced boiling [16], and CO_2 bubble generation in soda water [77] that each help flush loose powder from the part. After depowdering, the part should be dried prior to any additional processing.

6.3. Coating

Prior to sintering and/or infiltration it is possible to improve the surface finish of the part by coating the part with a layer of finer particles. This can be done using a polymer–particle paste of particles smaller than the bulk powder [38] or by slip casting a thin layer of fine particles (0.1–1 microns) onto the part [16]. Slip can be prevented from penetrating the pores of the part by selecting self-locking slip particles, precoating the construct, or saturating the construct with a liquid that will gel the slip [16]. The coating does not need to be the same material as the part, but the potential difference in thermal processing behaviors must be considered to reduce cracking problems.

6.4. Sintering

The two most common post-processing steps are sintering and infiltration. These steps can increase the strength of a part considerably, and in the case of infiltration, also significantly affect other bulk properties. First-stage sintering results in shrinkage of 1.5%–2% due to neck formation between particles [14], while sintering to full density results in greater than 15% linear shrinkage when starting with a 60% dense part [38]. Prior to sintering, the part can be settered by packing the part in a higher sintering temperature material to give the part support during thermal treatment. Settering is particularly useful for binders that thermally degrade and result in a temperature range where little is binding the part prior to the onset of particle sintering. The applicability of settering to high shrinkage sintering is limited since the support material may resist the dimensional changes of the part [14].

The major sintering parameters are material selection, particle size, sintering time, and sintering temperature. The printing process is dependent on the first two of these, while the thermal parameters are external to the 3DP process. Every material has specific sintering characteristics, but by using different particle sizes, mixtures, coatings, and sintering aids/inhibitors the designer can exert significant control over the required processing of the powder formulation. Metals, in particular, have considerable sintering flexibility. Varying the distribution of large and small particles combined with mixing metals of different liquid and solidus sintering characteristics can significantly affect the sintering temperature ranges and densification behavior of a powder [43]. The sintering temperature of a metal can also be raised by coating with a refractory material (for example, chromium electroplated on steel) or intentional oxidization (for example, SS at 400 °C–700 °C) [14]. The sintering behavior of ceramics is more difficult to alter, but sintering aids like tetraethylorthosilicate (TEOS) can benefit the process. During the sintering thermal cycle TEOS melts at a temperature lower than the sintering temperature of the ceramic and can flow and rearrange particles using surface tension forces [28]. Polymers can also be sintered, but special attention must be paid to the binder residue. The lower sintering temperatures of most polymers means the binder may not be thermally degraded and may remain in the part.

6.5. Infiltration

Infiltration is a way to achieve high density parts without the large shrinkage associated with sintering to full density [26]. Both low and high temperature infiltrations are possible depending on the part material and binding mechanism. The only constraint on the process is that the infiltrant must melt at a temperature below the melting point or solidus temperature of the bulk material so the part does not lose structure during infiltration [38]. An exception to this is when the powder is coated with a higher temperature

material (for example, carbon coated with a ceramic) so only the coating comes in contact with the infiltrant [78]. The preferred traits for melted infiltrants include sufficient fluidity and viscosity to flow through the part pores, and a low contact angle with the bulk material to make the infiltration more effective [47].

Low temperature infiltration is usually performed at or slightly above ambient and well below any phase-altering temperatures of the part. Example infiltrants include molten wax, varnish, lacquer, cyanoacrylate, polyurethane, and epoxy [58]. Infiltration is most commonly performed by dipping the part, but parts can also be infiltrated by aerosolizing the infiltrant and spraying the part [79]. For elevated temperature infiltration (for example, melted wax), it is important to preheat the part prior to infiltration. This prevents premature solidification of the infiltrant near the surfaces of the part and allows more complete infiltration.

High temperature infiltration requires control over the composition of the infiltrant as well as the thermal processing. Infiltration occurs at temperatures 20 °F–50 °F above the melting point of the infiltrant [13], and the part must be held at this temperature long enough for complete infiltration to occur. In many cases the infiltrant is an alloy that must be taken into account "because particles, especially if they are large, may not intermix homogeneously when they melt, and because certain elements may be more easily volatilized from elemental alloy powders, a different elemental alloy composition may be needed to produce a part that has the same composition as a part made from a prealloy" [52]. Alloy separation problems can be eliminated by gating, which consists of mechanically separating the infiltrant from the part until complete melting has occurred [38]. While infiltration is usually used to create composites, it is possible to make some homogeneous metal parts. A homogeneous metal part may be created using a melting point depressant (MPD) to create a lower melting temperature phase of the bulk powder, infiltrating the part, and then keeping an elevated temperature to allow the MPD to diffuse into the base powder to homogenize the part [38]. To avoid premature solidification due to diffusional solidification of the infiltrant, the infiltration rate can be increased by increasing the particle diameter and infiltrant surface tension, and decreasing the infiltrant viscosity and solid diffusivity [80]. Specific 3DP infiltration examples include infiltration of a gold powder skeleton with a gold eutectic [81], an alumina dental coping with dental glass [75], and carbon powders with silicon to form SiC–Si composites [21].

Part infiltration can be influenced by steps taken earlier in the 3DP process. Printing an infiltration stop material will prevent infiltration of certain areas of the part and aid in the formation of internal structures like cooling channels or internal voids [77]. Infiltration may also benefit from the incorporation of feeder channels or sprues [38], which can be directly printed using 3DP.

Infiltration is the last of the processing steps presented. Additional finishing steps can be performed to complete the fabrication of a 3DP part, but these are external to the core development of a new 3DP materials system.

7. Conclusions

This paper presents an organization of the steps involved in developing specific implementations of 3DP along with a review of currently available literature to support each of the steps in the development process. A thorough understanding of the complete 3DP process helps the user take advantage of the considerable material flexibility of 3DP and speed the development of new material and binder systems. The goal here is to provide a unified presentation of the overall state of the art along with links that provide practitioners with access to the specific sources of detailed information needed to realize new material combinations and characteristics via the 3DP process.

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