THE LIQUID-TO-SOLID TRANSITION
IN STEREODEPOSITION TECHNIQUES

R.S. Crockett, P.D. Calvert
University of Arizona, Tucson, AZ

Introduction

Stereodeposition is a broad category of Solid Freeform Fabrication techniques that accomplish the layerwise buildup of an object through the direct placement of bulk material. All stereodeposition techniques involve writing a path of liquid material, which rapidly undergoes a transformation to a solid. This transformation can occur by cooling, removal of solvent, or a catalyzed chemical reaction; the only requirement is that initial solidification provide sufficient change to support the next cross-sectional layer. Post-processing can later be performed on the object as a whole to achieve final properties, such as completion of polymerization or burnout of binder and sintering of ceramic particles.

This family of layerwise processing techniques lends themselves to the production of a wide range of materials, including functional ceramics[1], engineering polymers, and composites[2]. Beyond this, stereodeposition has the potential to produce complex, functionally gradient materials[3] and ultimately enable the chemical processing of exotic material systems which mimic biological processes[4]. The key to this flexibility is stereodeposition's ability to operate under a wide range of liquid-solid transformation rates. The first generation of stereodeposition processes have selected material systems with object precision and ease of operation as the driving goal. This leads to the extrusion of thermoplastic materials with a high viscosity (1000-10000 cps)[1,2] or to systems with a reaction rate $< 1 \ s^{-1}$.[5] The more interesting end of the spectrum for expanding the range of materials, however, is systems with low viscosity and low reaction rates combined with significantly higher shrinkages. In extending the use of stereodeposition from thermoplastics and other high-solidification rate materials, it is necessary to understand how the characteristics of a material system of interest impact the freeforming process. This paper presents current efforts at the University of Arizona to model the deposition and transformation in stereodeposition techniques, followed by a brief discussion on the impact of material characteristics on the operation of stereodeposition systems.

Stereodeposition Techniques and Solidification Strategies

The original and simplest method of rapidly transforming a bead from liquid to solid is through removal of heat. In the Stratasys Fused Deposition Modeling (FDM) process, a wax or low viscosity polymer in the form of a filament is melted and deposited, solidifying upon cooling. By using the polymer as a binder for ceramic particles, this process has been extended to produce ceramic greenbodies in the Fused Deposition of Ceramics (FDC) process[2]. Advanced Ceramics Research (ACR) employs a similar technique, using a high pressure (0.5 to 4.5 kpsi) extrusion apparatus to produce high molecular weight polymer objects and ceramic greenbodies from feed rods. In all of these processes, the liquid-solid transformation occurs quite rapidly. This transformation is determined by heat flow for glass-forming materials or by much slower crystallization kinetics in waxes and Nylon. Even in these cases, however, the time scale is probable less than 1 minute.

The Reactive Stereodeposition process[6], originally developed to produce ceramic objects, involves significantly slower transformation rates. In Reactive Stereodeposition, a highly-loaded ceramic slurry is dispensed through a syringe in an appropriate 2-D pattern; a sufficient binder polymerization rate is achievable by a catalyzed reaction, combined with rheology changes, to

rigidize the slurry sufficiently to support the weight of successive layers. Catalysis can be triggered by the activation of a component already present in the slurry. Depending on the type of polymer binder, the activation can be in the form of heat, light, or a change in pH. It is also possible to introduce a catalyst in a mixing chamber immediately before the slurry is deposited. This technique has been used by ACR to produce alumina and silicon nitride parts from slurries containing ceramic powders or inorganic fibers dispersed in liquid acrylic monomers[7], which are polymerized by dispensing on a heated surface.

A stereodeposition system developed at the University of Arizona[6] employs ethyl silicate, a metal alkoxide compound, as a binder. Rigidization is achieved initially by the rapid evaporation of ethanol and recovery from shear thinning during the deposition process. Gelation of the binder is then triggered by the addition of a base catalyst (NH_4OH) through a spray of ammonia water applied to the surface. Full curing takes hours, and is allowed to continue in the object as a whole by suspending the greenbody in a sealed container above a mixture of ethanol and ammonium hydroxide. This provides a wet, basic environment for the continuation of curing without drying. After curing is complete (approximately 24 hours), the environment is modified to allow for drying at a slow rate. This system has been used to produce silica, mullite, and fiber-reinforced borosilicate glass greenbodies.

In extending the Reactive Stereodeposition system to the slowest liquid-solid transformation rates, initial solidification must result primarily from rheology changes of the slurry, which are often sufficient to support the shape of a deposited bead for an extended period of time. In this case, polymerization of the binder can occur as a separate, later step. Thus the slurry's rheological properties, and especially the impact of shear thinning and solvent removal, become driving criteria for slurry development.

Modeling the Liquid-to-Solid Transition

Deposition and Bead Stability

Stereodeposition shares with other freeforming techniques a relationship between write speed and cross-sectional path area, with operational boundaries defined by the characteristics of the material. The flow of a viscous material through a deposition orifice (figure 1a) is controlled by Hagen-Poiseuille flow[8], in which flow rate (Q) is reduced for high fluid viscosity (η) and small orifice sizes (R) or long tip length (L) at a given deposition pressure (P_{GAGE}):

$$Q = \frac{\pi R^4 P_{gage}}{8 \eta L} \tag{1}$$

Once the material leaves the dispensing tip, conditions for bead stability during writing impose a limit to the head speed. For a given volume flow rate, bead cross sectional area is inversely proportional to head speed (figure 1b). As speed is increased, bead area is reduced; above a certain speed (equivalent to a minimum cross sectional bead area), the bead will tear, producing gaps in the final part. The minimum achievable area at the maximum head speed is a similar geometry to the problem of an axisymmetric liquid bridge[9], which is stable up to a height limit on the order of the square of the tip height above the surface divided by π:

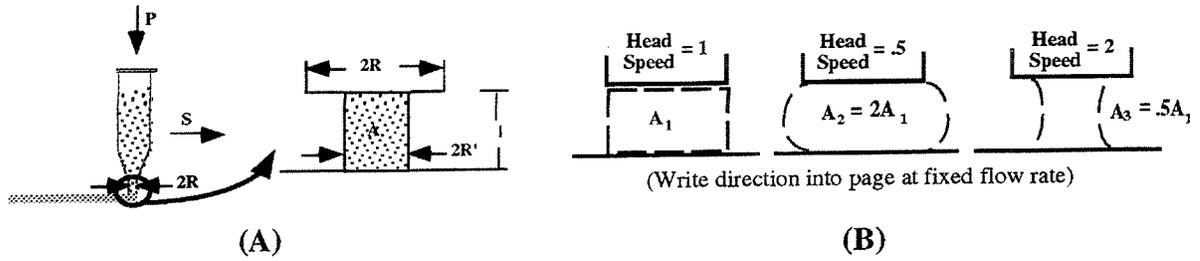$$A_{min} = 2lR' = \frac{l^2}{\pi} \tag{2}$$

258

Figure 1. Deposition geometry.

Combining equations (1) and (2), we have the imposed condition for depositing a continuous bead with a minimum cross sectional area:

$$\frac{\pi R^4 P_{gage}}{8\eta LS} > \frac{l^2}{\pi}$$

(3)

While liquid properties are not directly involved in the stability limit presented in equation (2), the impact of exceeding the stability limit and the ability of a material to "neck down" from R to R' varies based on the Weber number and the Reynolds number of the liquid[10]. The Weber number contains the magnitude of the surface tension, with low surface tension liquids less susceptible to forming individual droplets. Because it is also associated with splashing, the Weber number is an important parameter in the resolution of individual write paths in the 3-D Printing process[11].

Bead Spreading

If the deposited bead conforms to a Bingham-type rheology with an increasing yield strength caused by polymerization and solvent removal, it is possible to derive a differential equation for the rate of increase of bead width (S_{SL}).[12]:

$$\frac{dS_{SL}}{dt} = \frac{1}{\eta}\frac{A}{S_{SL}{}^2}\frac{\left(F(\theta) - F_Y(t,\theta)\right)}{l}$$

(4)

Here η is the liquid viscosity and A is the bead cross sectional area. The driving force for spreading per unit of bead length (F/l) and restraining force per unit of bead length (F_Y/l) are found by a force balance performed at the edge of the spreading bead (figure 2a). Substituting appropriate equations for forces and for the bead width in (4) produces an equation for the change in bead contact angle over time:

$$\frac{d(\phi)}{dt} = \frac{A}{R^2\phi}\frac{\gamma_{LV}}{\eta R}\left[\frac{(1-\cos\theta)}{\phi} - \frac{\tau_Y(t)R}{\gamma_{LV}}\right]$$

(5)

In this equation, γ_{LV} is the surface tension of the deposited liquid, τ_Y is the liquid yield strength, and R is the radius of curvature of the surface onto which the bead is dispensed (an individual bead in the previously deposited layer). Geometrical constraints (figure 2b) produce a relationship between ϕ and θ:

$$\left(\frac{\sin\theta}{\tan\phi} + \cos\theta\right)^2\left(\frac{2A}{R^2} + \phi - \sin\phi\cos\phi\right) = \theta + \phi - \sin(\theta+\phi)\cos(\theta+\phi)$$

(6)

259

$$\tau_Y A_{SL}(\theta) + [\tau_{Evap}(t) + \tau_{Gel}(t)] A_{SL}(\theta)$$

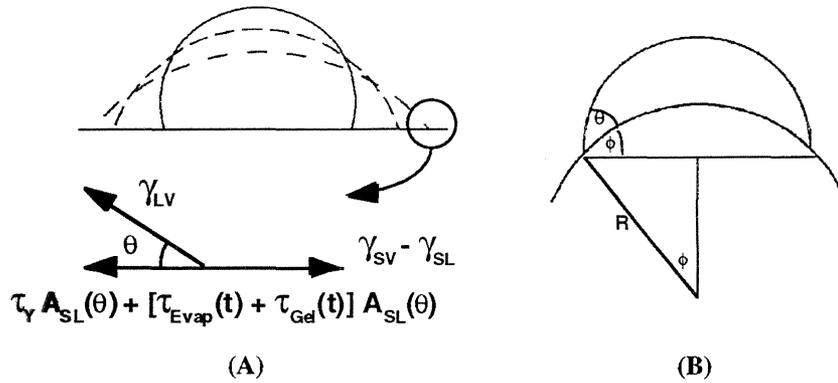(A)   (B)

Figure 2. Force balance and bead geometry.

Solidification Cases

For the purpose of further simplifying the model, the spectrum of solidification rates associated with existing stereodeposition systems can be classified into 0, moderate, and fast, corresponding to no property changes, surface property changes, and bulk property changes of the liquid during bead spreading. The simplest case of equation (5) occurs when the yield strength of the liquid is constant and no property changes occur during the spreading process. This is the situation that occurs in the slowest Reactive Stereodeposition systems. The bead will continue to spread at a rate controlled by surface tension, viscosity, and bead geometry. It will stop at a final contact angle occurring when $d\phi/dt = 0$:

$$\frac{(1-\cos\theta)}{\phi} = \frac{\tau_Y R}{\gamma_{LV}}$$

(7)

Under conditions of moderate diffusion rates, the yield strength of the liquid is increased in a surface shell, without changing the bulk properties of the liquid. This occurs in chemically reacting systems or when there is a loss of solvent from the surface during dispensing. In this case, the bulk viscosity remains constant, but the yield strength increases with time due to the formation of a "shell" which increases in thickness. The final contact angle now depends on time, based on the permeability of the solidifying shell (P) and the driving force for mass transfer (ΔC):

$$\frac{1-\cos\theta}{\phi} = \frac{\tau_Y R}{\gamma_{SL}}\left[1 + \frac{(2P\Delta Ct)^{\frac{1}{2}}}{R\phi}\left(\frac{\tau_{Y,solid}}{\tau_Y} - 1\right)\right]$$

(8)

Permeability is usually associated with a gas passing through a film and is expressed, for example, as cm^3 gas at standard temperature and pressure passing per second through 1 cm^2 of a membrane 1 cm thick when the pressure difference across the membrane is 1 cm of mercury. If a linear relationship exists between external vapor pressure and a corresponding equilibrium concentration within the membrane, permeability can be expressed in terms of the more fundamental diffusion coefficient, which has units $cm^2 s^{-1}$. The driving force for mass transfer is either a concentration gradient or capillary pressure gradient, depending on the characteristics of the solidifying material.

If the diffusion is fast enough, the bulk properties of the liquid change appreciably during spreading. This is the case with solidification due to thermal diffusion, such as occurs in the cooling of a thermoplastic from a melt (FDM). A typical way to mathematically treat this case is to define a "gel time" at which the viscosity and/or yield increases dramatically. In this situation, the liquid properties would be treated as a step funtion.

There are a number of key parameter groups which can be identified from the spreading model presented above. In the absence of property changes, the final contact angle of a deposited bead is controlled by:

$$\alpha = \frac{\tau_Y R}{\gamma_{LV}} \tag{9}$$

Because of its use in rheology discussions, it is useful to introduce the "index of plasticity":

$$\beta = \frac{\tau_Y}{\eta} \tag{10}$$

With this definition, the rate of bead spreading is controlled by:

$$\frac{\alpha}{\beta} = \frac{\tau_Y R}{\gamma_{LV}} \times \frac{\eta}{\tau_Y} = \frac{\eta R}{\gamma_{LV}} \tag{11}$$

This parameter grouping is the same as that which controls the rate in amorphous material sintering processes[13] and capillary penetration of liquids[14].

Finally, the time-dependent solidification or "strength diffusion" term becomes:

$$\delta = \frac{(2P\Delta C)^{\frac{1}{2}}}{R}\left(\frac{\tau_{Y,solid}}{\tau_Y} - 1\right) \tag{12}$$

Using these groupings, the full solution to bead spreading is:

$$\frac{d(\phi)}{dt} = \frac{A}{R^2 \phi}\frac{\alpha}{\beta}\left[\frac{(1-\cos\theta)}{\phi} - \alpha\left[1 + \frac{\delta t^{\frac{1}{2}}}{\phi}\right]\right] \tag{13}$$

After the first few deposited layers, the system will achieve a "system contact angle", where the newly deposited bead spreads until it's final radius equals the radius of the bead onto which it was deposited. Under these equilibrium conditions, R is a function of the square root of A, eliminating one system variable. The full bead spreading solution thus involves a 3-dimensional material "parameter space" of α, β, and δ. Current work at the University of Arizona is on verifying this model, and results will be presented at next year's symposium.

## The Effect of Material Parameters on Process Results

Generalizing about the parameter groupings derived above, alpha represents a liquid's resistance to motion. It is in effect a ratio of the restraining force to the driving force, thus a large alpha represents a system similar to extrusion, where flow is limited. Beta determines the system's response time, with a small beta (high viscosity) indicating a "sluggish" system. One example of how these parameters interact to effect process results is the phenomenon of casteling, wherein irregularities in deposited lines grow into large peaks and troughs in the course of forming multiple

Equilibrium Contact Angle
vs. Alpha, Delta

Θ
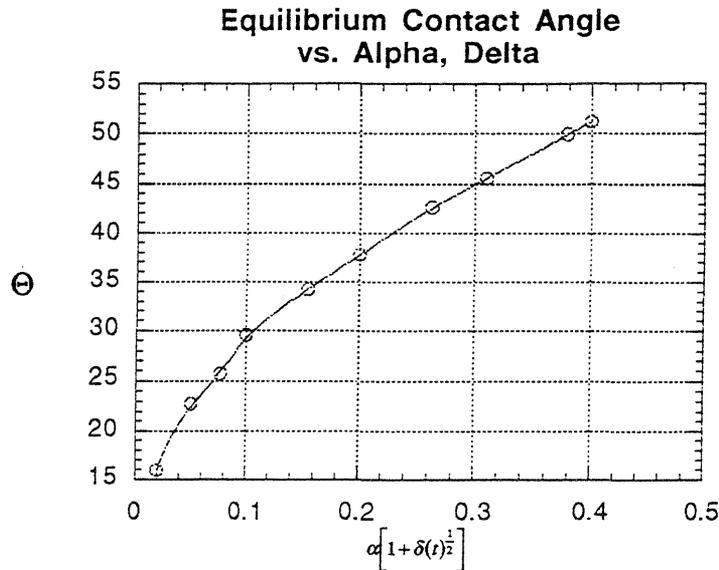
Figure 3. Dependence of system contact angle on material
parameters.

layers. This occurs under either low alpha (bead tears easily), or high beta (bead cannot respond to disturbances rapidly enough).

An important relationship is the effect of beta on spreading time, which in turn determines the impact of delta on total liquid property changes during bead spreading. Figure 3 presents a plot of system contact angle vs. alpha, delta, and spreading time (and thus beta) as determined by the model. It can be seen from this figure that the larger any of these three parameters, the larger the resulting system contact angle. The system contact angle determines the ultimate precision of the part in a direct tradeoff between path width and layerwise resolution (figure 4b). A bead with a cross-sectional area of 1 mm² which achieves a contact angle of 5° will result in a path width of 3.9 mm and layerwise resolution (layer thickness h in figure 4a) of 510 μm. Increasing the contact angle to 40° by increasing alpha, delta or beta reduces the path width to 2.4 mm at the expense of an increased layer thickness of 820 μm. Also associated with contact angle is the *surface roughness*, the difference between the maximum and minumum radii of the deposited beads (figure 4a). The cases presented above have an inherent roughness of 17 and 70 μm, respectively. It is important to note, however, that in producing a solid, the outer surface (the circumference of a layer), may be written with more care than the interior of the layer. Line width is thus not necessarily the limiting factor to build time.

(A)   (B)
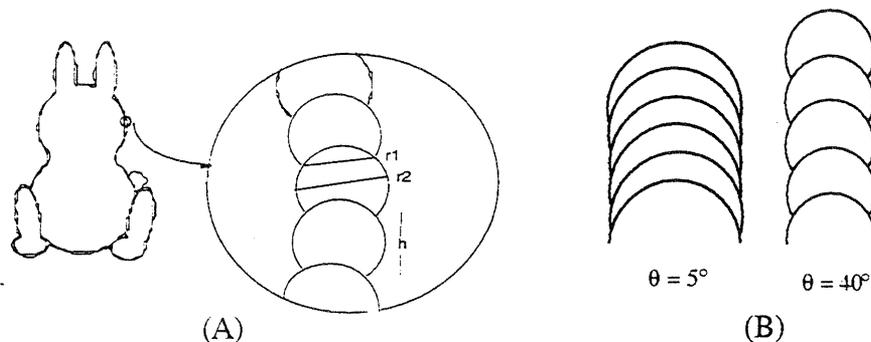
Figure 4. (A) Resolution (h) and surface roughness (r2-r1).
(B) Dependence on contact angle.

262

**5 micron Silica in Ethyl Silicate
72 h mill time**
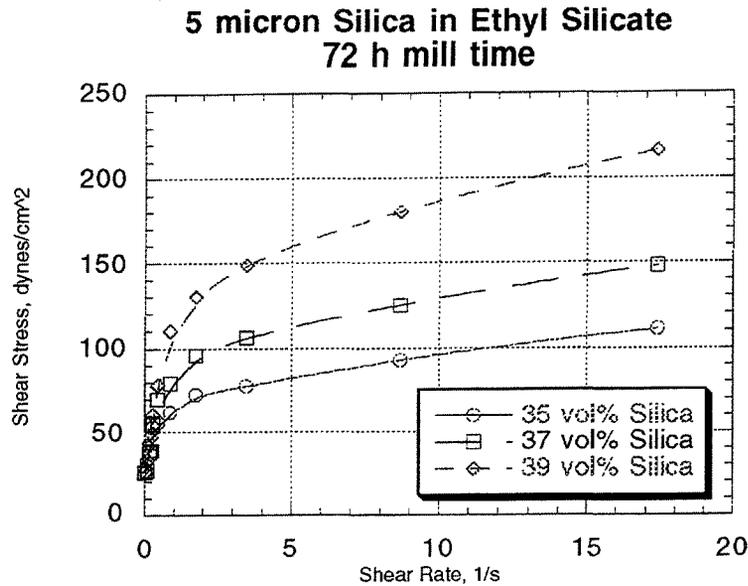
Figure 5 - Rheology of typical ceramic slurry used for reactive stereodeposition.

A low beta relative to alpha is useful in controlling the contact angle and providing time flexibility. The downside to this, however, is the lack of flow which can create diamond-shaped flaws between individual paths. A strategy we use extensively in our reactive stereodeposition process to achieve a desirable amount of flow and a reasonable contact angle is to adjust the rheology to produce a shear-thinning, Bingham plastic liquid with a yield point.

For our systems, at least, this is achieved by the addition of a solvent to thin the liquid plus 1-2 vol% fumed silica to develop a shear-dependent rheology (figure 5); the yield strength of these liquids is established at 5%-10% of the ratio of liquid surface tension to bead cross-sectional area. Viscosities on the order of 100 cps during deposition under shear rates of 100 s^{-1} allow for dispensing at 10 psi. The fluid viscosity then rapidly increases to greater than 10^4 cps during the spreading, as the shear rates drops below 10^{-1} s^{-1}. This allows a reduced spreading rate and sufficient yield to control the final contact angle. The extreme extension of this strategy is where a stable contact angle is reached after a period of flow by recovery from shear thinning without any solidification occurring; curing is then performed as a separate step on the surface of an entire layer.

Clearly, solidification during bead spreading modifies the impact of the liquid properties and thus the final contact angle of a bead. Solidification rate also controls the time required between placement of adjacent beads and layers to prevent further shape changes, as well as the inter-layer adhesion and shape limitations of the final object. An obvious objection to a freeforming approach is the long processing time needed to react a sequence of layers. Our rule of thumb has been that reaction should be complete to the point of solidification within one minute for a layer. This gives reasonable process times for layers which are 0.1-1mm thick. A typical diffusion coefficient in liquid is 10^{-5}-10^{-6} cm^{2}sec^{-1}, which corresponds to a diffusion length of 0.1-0.5 mm in a minute. This suggests a maximum layer thickness in this range for chemical reactions involving diffusion out of products or loss of solvent. If diffusion, rather than reaction rate, is limiting it should be possible to write thinner layers faster to obtain faster overall processing. Thermal diffusion is generally much faster than mass diffusion and is unlikely to limit the forming rate in materials that solidify by cooling.

Rapid reaction will result in adiabatic heating of the layer, especially in monomer-rich systems with poor thermal conductivity. We have observed waves of reaction, which we attribute to such thermal autoacceleration, moving through partly-formed parts. Thus self-heating can limit the overall rate at which material is deposited. With our system, at least, too rapid reaction, in relation to the time to write a layer, also results in poor interlayer bonding and later delamination.

This paper has focused on the importance of understanding the impact of material properties on the stereodeposition process, specifically in the critical liquid-solid transition. While we have touched on some of the key issues, there is still much to be understood. The ultimate motivation, however, is that a solid understanding will increase the range of material systems compatible with stereodeposition techniques, allowing this method to produce increasingly novel materials.

ACKNOWLEDGMENTS

REFERENCES

[1] K. Stuffle, A. Mulligan, P. Calvert, J. Lombardi, "Solid Freebody Forming of Ceramics from Polymerizable Slurry", *Proceedings of the Solid Freeform Fabrication Symposium*, University of Texas at Austin, September, 1993. pp.60-63.

[2] M.K. Agarwala, *et. al*, "Structural Ceramics by Fused Deposition of Ceramics", *Proceedings of the Solid Freeform Fabrication Symposium*, University of Texas at Austin, August, 1995. pp.1-8.

[3] G.E. Hilmes, "Recent Developments in Extrusion Freeform Fabrication (EFF) Utilizing Non-Aqueous Gel Casting Formulation", to be published in the *Proceedings of the Solid Freeform Fabrication Symposium*, University of Texas at Austin, August, 1996.

[4] P.D. Calvert and R.S. Crockett, submitted to *Chemistry of Materials*.

[5] See, for example, rate discussions for Selective Laser Sintering (p 55), Stereolithography (p. 134), and Shape Deposition Modeling (p.118), *Proceedings of the Solid Freeform Fabrication Symposium*, University of Texas at Austin, August, 1995.

[6] R.S. Crockett, *et. al.*, "Predicting and Controlling Resolution and Surface Finish of Ceramic Objects Produced by Stereodeposition Processes", *Proceedings of the Solid Freeform Fabrication Symposium*, University of Texas at Austin, August, 1995. pp. 17-24.

[7] P. Calvert, R. Crockett, J. Lombardi, J. O'Kelly, K. Stuffle, "Extrusion Methods for Solid Freeform Fabrication". *Proceedings of the Solid Freeform Fabrication Symposium*, University of Texas, Austin, August 1994. pp. 50-55. 1994.

[8] White, Frank M., Fluid Mechanics, McGraw-Hill Book Company, New York, 1986, p305.

[9] Middleman, Stanley, Modeling Axisymmetric Flows, Academic Press, San Diego, 1995. p. 173.

[10] *ibid*, p. 112.

[11] M.J. Cima, *et. al.*, "Ceramic Components from 3-D Printing", Presented at the 98th Annual American Ceramic Society Meeting, Indianapolis, April 14-17, 1996.

[12] R.S. Crockett, "The Liquid-to-Solid Transition in Stereodeposition Techniques", University of Arizona dissertation, in preparation.

[13] Sherer, G.W., "Viscous Sintering of Inorganic Gels", pp. 265-300 in Surface and Colloid Science, vol. 14, ed. E. Matigevic. Plenum Press, New York, 1987.

[14] Reed, James, Introduction to the Principles of Ceramic Processing, John Wiley & Sons, New York, 1988. p. 24.