PREDICTING AND CONTROLLING RESOLUTION AND SURFACE FINISH OF CERAMIC OBJECTS PRODUCED BY STEREODEPOSITION PROCESSES

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Introduction

Stereodeposition techniques are well suited for the Solid Freeform Fabrication of dense ceramic components. As opposed to forming a pattern in a particle bed or polymer bath, stereodeposition processes deposit material directly onto the previously created layer. The key to stereodeposition is a material's ability to be dispensed as a fluid, yet rapidly stiffen to hold the shape of the object. This is accomplished by either solidification of a thermoplastic binder upon cooling from a melt *(Fused Deposition)* or by polymerization of a binder *(Reactive Stereodeposition)*. We are developing both techniques for the production of functional ceramic and engineering polymer objects.

A key issue in developing a successful stereodeposition system is controlling the rate of bead transformation from liquid to solid. Control is critical to achieving high resolution and low surface roughness of the finished product, but is made complex by the large number of parameters involved. These include *binder parameters* (surface tension, gelling characteristics), *slurry parameters* (viscosity, particle loading and size distribution), and *process parameters* (deposition rate, temperature). Current efforts at the University of Arizona are focused on modeling and controlling the deposition and transformation of ceramic slurries used in the Reactive Stereodeposition process.

Fused Deposition

Advanced Ceramics Research (ACR) is developing the Fused Deposition process under license from Stratasys, Inc. to produce objects useful in a wide range of applications. In the Stratasys Fused Deposition process, a wax or low viscosity polymer in the form of a filament is melted and deposited on a cold surface where it solidifies upon cooling. ACR has adapted the process to a high pressure extrusion apparatus which is compatible with a variety of materials. To produce ceramic objects, ceramic powder is blended with polymer binder in a high shear mixer. After mixing, the blend is compression molded into a cylindrical feed rod. Non-ceramic filled feedrods do not require high shear mixing; they are compression molded at the appropriate temperatures to form single-component polymer feed rods. Objects are drawn in AutoCAD and sliced into a series of two dimensional layers. This information is used to generate a continuous path for material extrusion. Operating pressures during extrusion range from 0.5 to 4.5 kpsi. The inner diameter of the extrusion nozzle is approximately 0.3mm.

We were able to fabricate parts from engineering thermoplastics such as polyetheretherketone (PEEK), polycarbonate and PMMA. Fiber filled grades of PEEK and polycarbonate were used to produce composite objects. In addition, polylactic acid/polyglutamic acid, a biologically resorbable copolymer, was processed for possible uses in manufacturing biomedical implant devices.

Preliminary mechanical testing was performed on free-formed tensile specimens as a function of material and bead orientation. Test bars were formed with the main deposition trajectory both parallel to the test direction and across the test direction. Tensile testing was performed as per ASTM D638. The mean results are summarized in Table 1 and compared to manufacturers specifications for bulk material. Samples were not machined prior to testing.

Table I.

Material	# of Specimens Tested	Orientation	Young's Modulus E GPa		Breaking Strength s_{Br} MPa		Elongation To Break (%)	
			Exp	Manf	Exp	Manf	Exp	Manf
PEEK	3	‖	1.683	3.6	58.77	100	3.335	50
	3	⊥	1.778	3.6	87.84	100	5.323	50
PEEK 30% CF*	1	‖	9.397	13	256.5	233	2.990	1.5
	3	⊥	3.561	13	123.8	233	3.57	1.5
Polycarbonate	7	‖	1.081	2.34	64.33	70	8.682	130
	6	⊥	1.017	2.34	46.43	70	5.642	130
Polycarbonate 30% GF**	8	‖	3.043	7	105.7	130	3.778	3.0
	4	⊥	1.461	7	60.91	130	5.771	3.0
PMMA	5	‖	1.333	3.3	23.24	41	1.388	1.8

‖ = Test Direction Parallel To Bead Direction

⊥ = Test Direction Perpendicular To Bead Direction

Mechanical Testing Parameters: Instron Model 1011; Strain Rate = .2 in/s; Load Cell=1000lb; Vertical specimen loading; Wedge-action type grip; *CF = Carbon Fiber; **GF = Glass Fiber

The tensile moduli of the unfilled polymers are all low when compared to values expected for conventionally formed glassy polymers, which typically have moduli of around 3 GPa. This lower modulus may be due to lubricants and degradation products from the compression molding and extrusion steps. The fact that the moduli show no effect of bead orientation suggests that porosity and reduced adhesion between lines are not factors, although some effect had been expected.

The fiber-filled polymers show a large influence of write direction on modulus. This is believed to be due to fiber orientation parallel to the write direction, in agreement with microscopic observations on ceramic systems[1]. The mechanical properties suggest that fiber orientation follows the writing direction.

Elongation to break is very sensitive to surface finish in the notch-brittle engineering thermoplastics. Hence, the low elongations are not surprising for these unpolished samples. Though breaking strengths would also be expected to be sensitive to surface or internal flaws, the measured values are generally in agreement with published data.

Ceramics have also been fabricated by Fused Deposition from powder filled rods to make a green body which is then fired. Alumina, zirconia and silicon nitride have been dispersed in binder and extruded to form a number of parts including a model oxygen sensor and a temporal mandibular joint (TMJ) prostethic device. Alumina and zirconia green bodies were sintered under pressureless conditions.

Reactive Stereodeposition

The Reactive Stereodeposition process is illustrated in Figure 1, below. In Reactive Stereodeposition, a highly-loaded ceramic slurry is dispensed through a syringe in an appropriate

2-D pattern; a catalyzed chemical reaction rigidizes the slurry sufficiently to support the weight of successive layers, allowing the object to be built up one cross-sectional layer at a time. The result after drying is a ~50% dense ceramic greenbody which can later be sintered to full density.
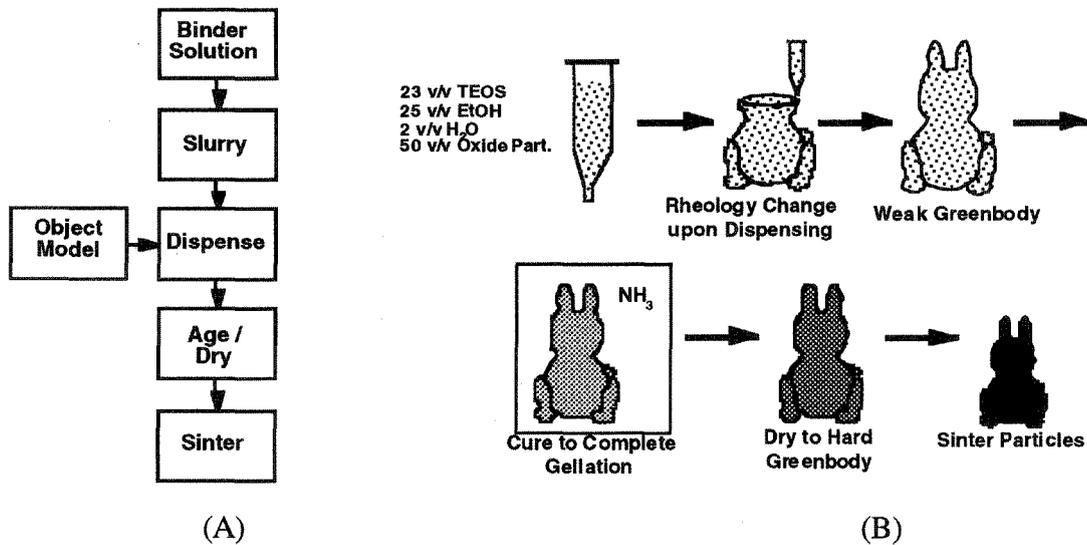

(A)   (B)

Figure 1. (A) Reactive Stereodeposition Process. (B) Alkoxide Binder Example.

This technique has been used to produce alumina and silicon nitride parts from slurries containing ceramic powders or inorganic fibers dispersed in liquid acrylic monomers[2]. A low-pressure stereodeposition system[3] has been used to produce silica, mullite, and fiber-reinforced borosilicate glass objects. In this case, the extruded slurry contains inorganic powder in solvent plus liquid silicon alkoxide.

Reactive Stereodeposition systems are compatible with highly loaded slurries, and thus are capable of producing greenbodies with a higher inherent density than is achievable with powder bed techniques. Typical alumina objects produced using this method achieved green densities 60% of theoretical, enabling them to be sintered to full density under pressureless conditions.

Reactive Stereodeposition systems also allow for microstructure flexibility. By dispensing different slurries through multiple nozzles, it is possible to locally modify the ceramic matrix and add fiber reinforcement to form unique composites and functionally gradient materials (Figure 2).
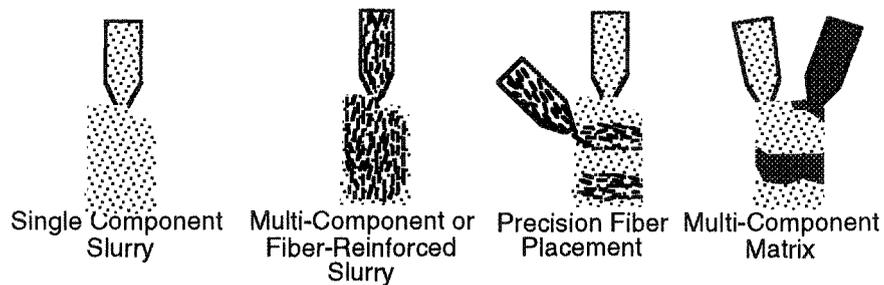

Single Component   Multi-Component or   Precision Fiber   Multi-Component
Slurry   Fiber-Reinforced   Placement   Matrix
                     Slurry

Figure 2. Microstructure Flexibility.

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Binder

The reactive stereodeposition process developed at the University of Arizona employs ethyl silicate, a metal alkoxide compound, as a binder. Ethyl silicate is a partially condensed oligomer of tetraethoxysilane (TEOS). The oligomer used in this work has an average molecular weight of 610 g/mol and will condense to 40 wt% silica upon complete densification. TEOS, on the other hand, condenses to only 29 wt% silica upon densification. The oligomer is used as opposed to the monomer to reduce shrinkage due to loss of chemically bound solvent and because ethyl silicate has previously proven useful in binding refractory powders through slip casting.[4,5]

Ethyl silicate reacts with water in the presence of an acidic or basic catalyst to form a continuous inorganic network or gel. In using ethyl silicate as a binder, the resulting Si-O-Si network remains in the object throughout the drying and sintering processes, in practice contributing ~3-10 vol% of amorphous silica to the ceramic matrix. This results in a higher effective greenbody loading, produced by a material which promotes either viscous or liquid-phase sintering and thus helps enable pressureless sintering of the ceramic object. Additionally, because gelation is a room-temperature curing process, there is less chance for warpage due to localized temperature gradients. There are also fewer burnout problems during the sintering phase, as there is less material actually leaving the object.

Slurry

To create a ceramic slurry, dry oxide powders are added to a carrier solvent (ethanol) which contains the ethyl silicate. The volume ratio of these components is defined by a tradeoff between ease of dispensing and rate of slurry rigidization. Reactive Stereodeposition requires the slurry to be fluid enough to deposit at low pressures (5-20 psi), yet harden sufficiently once on the surface to support the weight of successive layers. Additionally, it is desirable to achieve the highest particulate loading possible for improved densification during sintering. Thus the slurry's rheological properties, and especially the impact of shear thinning, become driving criteria for slurry development.

To achieve the required loading, the slurry can be deflocculated by organic dispersants such as phosphate esters or Menhaden fish oil[6]. Particulate loadings of greater than 50 vol % are readily achievable with a well-matched deflocculant and carrier liquid. An example slurry composition is provided in Table 2.

Table 2

Component	Weight %
Pyrex Powder (-325 mesh)	54.7
E-Glass Fiber	18.8
Ethyl Silicate	14.3
Ethanol	11.1
Dispersant	1.1

Dispensing

For dispensing, the slurry is placed in a pressurized syringe mounted on the head of an Asymtek model 402 benchtop dispensing system (Figure 3) and deposited through an 18-25 gage needle. Motion control is provided by an IBM PC, which handles all aspects of modeling and dispensing in a single integrated program running under AutoCAD Release 12. The AutoCAD AME package

provides modeling and object slicing functions, while software routines written in C provide overall control of dispensing operations, converting the AutoCAD data into Asymtek motion commands and issuing machine control statements.
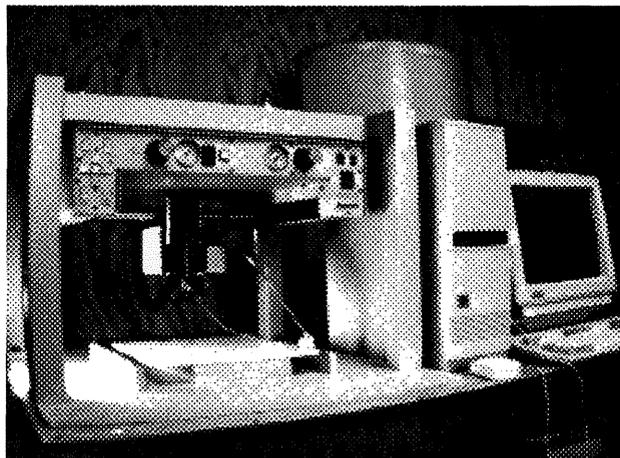

Figure 3. Deposition System

Once the slurry has been deposited, it must rapidly solidify. This is achieved initially by the rapid evaporation of ethanol during the deposition process. Gelation is then triggered by the addition of a base catalyst (NH_4OH) through a spray of ammonia water applied to the surface.

Unreinforced slurries are weak, thus to prevent cracking and allow handling, the greenbody must be further cured without allowing the surface to dry. The wet greenbody is placed in a sealed container, suspended above a 50/50 volume 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.

Alternatively, by adding fibers to the slurry (~25 vol%), it is possible to dry the greenbodies at an increased rate. The fibers give the partially-cured part the extra strength required to withstand drying stresses.

The final step in the process is the sintering of the dried greenbody. A typical firing schedule begins with a two hour ramp to 200 °C. This temperature is held for two hours to allow non-chemically bonded water and ethanol to evaporate. This is followed by a four hour ramp to 900 °C and another hold to ensure that all organics are removed. Finally, the temperature is slowly ramped to 1100-1500 °C (depending on the ceramic composition) to complete sintering.

Process Modeling and Control

The key requirement in the Reactive Stereodeposition process is that the bead rapidly transform from liquid to "rigid", where it can support it's own weight at an equilibrium contact angle $0 < \theta < 180$ (Figure 4, below).
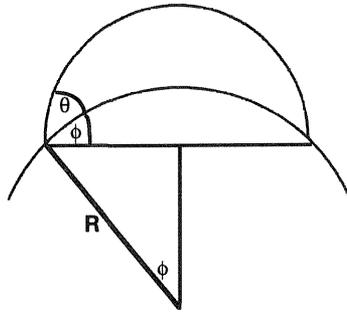
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Figure 4. Bead Geometry (Cross Section).

This solidification results from a combination of 1) rapid polymerization of the binder, and 2) rheology changes in the slurry. A sufficient polymerization rate is achievable by a catalyzed reaction of the binder, which 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.

Assisting the solidification process are rheology changes which occur as solvent rapidly evaporates due to the large amount of surface area introduced during the dispensing process. This forms a thin, temporary skin on the slurry bead. The rheology changes in this skin due to the increased effective particle loading are often sufficient to support the shape of the bead for an extended period of time. In the extreme, initial solidification of the slurry bead is accomplished entirely by the rapid removal of solvent, and polymerization of the binder occurs as a separate, later step in the Reactive Stereodeposition process.

Although rigidization can be achieved in a variety of ways, it is critical for the appearance of the final greenbody to control the resulting equilibrium contact angle. As seen in Figure 5, *resolution* (the thickness of an individual layer) and *surface roughness* (the "bumpiness") are directly related to the equilibrium contact angle between the slurry bead and the previously deposited layer. Thus predicting and controlling the equilibrium contact angle is an important part of slurry development.
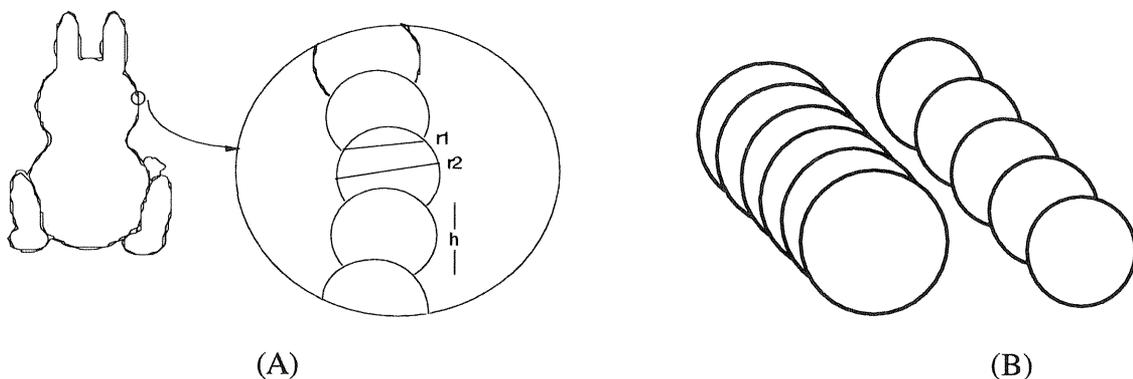

(A)   (B)

Figure 5. (A) Resolution (h) and Surface Roughness (r2-r1). (B) Dependence on Contact Angle

Equilibrium contact angle depends on the rate of bead transformation from liquid to solid. This in turn is a complex function of *binder parameters* (surface tension, gelling characteristics), *slurry parameters* (viscosity, particle loading and size distribution), and *process parameters* (deposition rate, temperature). The relationships between these parameters can be quantified and modeled by a time-dependent force balance at the edge of the spreading bead (Figure 6).
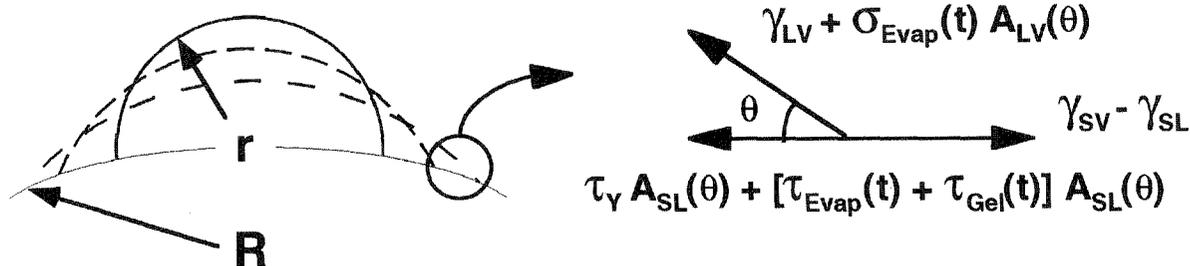
Figure 6. Contact Angle Modeling.

If the slurry bead conforms to a Bingham-type rheology with an increasing yield strength caused by gelation and solvent removal, it is possible to derive a differential equation for the rate of increase of bead width (S_{SL}).[7]:

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

(1)

where the driving force for spreading, F, depends on the surface tension of the slurry liquid; F_Y contains the evaporation and gelation terms; the slurry viscosity, η, controls the process rate. This equation provides a predictive tool to aid both in the development of slurries and in selection of deposition conditions for the Reactive Stereodeposition process. For example, a predictive plot such as that shown schematically in Figure 7, below, can be prepared to show the effect of gellation rate and solvent evaporation rate on the equilibrium contact angle θ_{eq} for a specific slurry composition. As either evaporation rate or gellation rate is increased, the equilibrium contact angle will increase, resulting in a part with lower resolution and greater surface roughness. Either deposition conditions or the slurry composition can be adjusted to achieve the desired appearance of the final object.
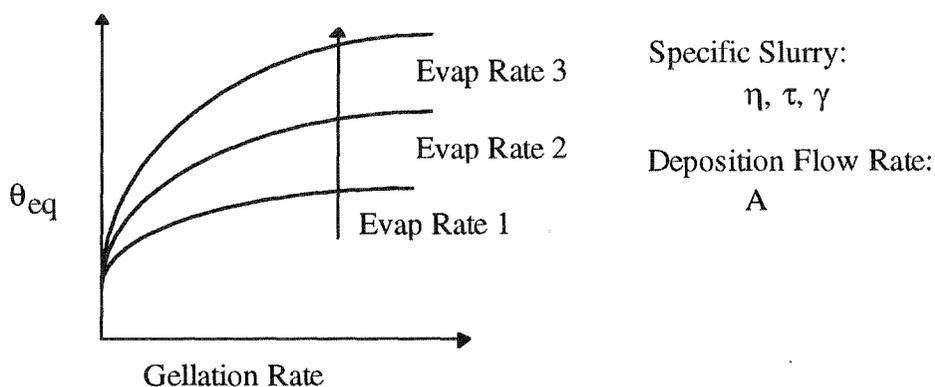

Figure 7.

Current work at the University of Arizona is focused on developing and evaluating this model for silica slurries in an ethyl silicate binder.

ACKNOWLEDGMENTS

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