

Stereolithography of Ceramics and Metals

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Abstract

Direct stereolithography fabrication of ceramic and metal components is reviewed with emphasis on progress made toward three important aspects of the technology: 1) the physical/mechanical properties achievable, including the range of materials that can be utilized; 2) the dimensional accuracy of the process, including the level of surface roughness; and 3) the process economics and delivery times achievable. Strength data on a variety of stereolithography fabricated metal and ceramic components is summarized. Dimensional accuracy and surface roughness issues are discussed and a cost analysis for fabricating two representative ceramic parts is presented.

Introduction

Advances in stereolithography resins and build techniques have enabled the fabrication of models with improved properties, higher accuracy and excellent surface finish while maintaining high build rates. Based on these advantages a number of secondary processes have been developed which use the stereolithography (SLA) model as a key component in rapid tooling methods such as silicone RTV (room temperature vulcanization), Direct AIM™ (SLA fabrication of epoxy injection molding tooling for short runs) and 3D Keltool™ (hard tooling for long runs). Further expansion of the utility of stereolithography can be achieved if it is applied to the direct fabrication of functional ceramic and metal components. Several groups[1,2,3,4,5] have reported on the feasibility of using liquid photocurable resins filled with suspensions of sinterable metal and ceramic powders in a stereolithography machine to produce green state components. Binder removal followed by sintering, or other densification method, has resulted in ceramic and metal objects with high density and properties comparable to conventionally processed materials. This processing route offers a number of benefits, the most universal of which is the freedom from the cost and lead times associated with part specific tooling.

The extent to which any new component fabrication process is accepted and used commercially depends substantially, although not totally, on four aspects of the process: 1) the physical/mechanical properties achievable, including the variety of materials that can be utilized; 2) the dimensional accuracy of the process, including surface finish achievable; 3) the range of geometrical complexities and component sizes which can be produced; and 4) process economics and lead times relative to conventional fabrication methods. This paper describes progress made by Ceramic Composites, Inc. and others in these critical aspects of stereolithography-based fabrication of ceramics and metals.

Process Overview

Figure 1 shows a flow chart of the process. A ceramic or metal resin (also referred to as an ink) is prepared by mixing the constituents using a ball/roller mill or similar method. The components of the resin include a monomer/initiator package which provides photocurability, dispersants to maintain low viscosities at high solids loadings and the sinterable ceramic or metal powder. Other additives may be used to modify rheology of the ink, enhance the cure properties, ease binder removal and/or improve the properties of the as-sintered parts.

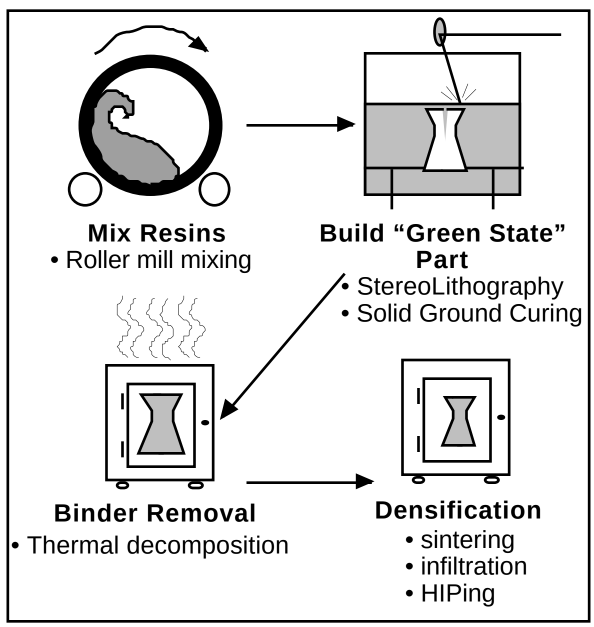

Figure 1. Process flow chart for stereolithography fabrication of ceramics and metals.

The resin is then used in a stereolithography or similar apparatus to selectively cure, layer-by-layer the desired object. Once the uncured resin is cleaned from the part, it is thermally processed, during which the photopolymer binder is removed by thermal decomposition and the part is sintered to impart high density and give the desired metal or ceramic properties. The process is essentially a ceramic powder processing or powder metallurgy technique analogous to ceramic/metal injection molding, slip casting, gelcasting, die pressing, etc.; with the primary difference and advantage being the direct use of stereolithography which provides accurate forming of complex shaped objects without the use of part specific molds, dies or other tooling.

The next section describes the requirements for achieving physical/mechanical properties comparable to conventionally processed materials and summarizes the results achieved by CCI and others in a variety of ceramics and metals. The following section covers the issues related to imaging accuracy and surface roughness and the effect of high solid loadings on these characteristics. And finally, a cost analysis of the process is presented which compares the cost of fabricating two representative ceramic parts by conventional methods and by stereolithography.

Physical/Mechanical Properties

In powder processing and consolidation of ceramics and metals, achieving high green density is generally a priority to produce materials of good dimensional and structural integrity. For stereolithography processing this requires that the inks have a high solids loading. Typically 50 vol% sinterable powder will suffice, but higher loadings are desired to: 1) minimize strength limiting porosity in the sintered products; 2) to speed debinding and reduce the risk of part disruption during binder decomposition; and 3) to reduce sintering shrinkage and the distortions and cracking which can result. Solid loadings of fine grained ceramics above 35 vol% typically require the use of a dispersant to manage particle-particle interactions and maintain a low viscosity. Tailoring the dispersant package to the monomer medium and the surface chemistry of the inorganic particles enables loadings approaching 60 vol% using micron size particles while maintaining viscosity below ~5,000 cPs. If care is taken to preclude impurities, eliminate air bubbles in the ink and avoid laminar defects during part building and processing, then typical ceramic sintered densities (e.g. 93–99% theoretical) can be achieved by using stereolithography as a green state shape forming method.

All additive freeform fabrication techniques are laminar processes, i.e. built up layer-by-layer and hence are susceptible to laminar defects. In stereolithography-based approaches, laminar defects are prevented by achieving good interlayer bonding and managing the cure shrinkage such that residual stresses from layer to layer do not accumulate. Optimization of the monomer mixture and the photoinitiator package to enable good through cure and bonding at the interface while minimizing and to some extent accommodating cure shrinkage, results in good interlayer bonding and low risk of delamination during debinding. Figure 2 shows the fracture surface of a green state stainless steel sample made with Ceramic Composite's 55 vol% stainless steel ink. The sample consists of 52 layers, each applied 0.001" thick and photocured under an ultraviolet flood lamp through a photomask. Good interlayer bonding was achieved in this sample as evidenced by the fact that fracture did not expose any weak laminar interfaces. Typically, debinding and sintering of a well bonded sample like this one will proceed without generating strength limiting laminar defects.

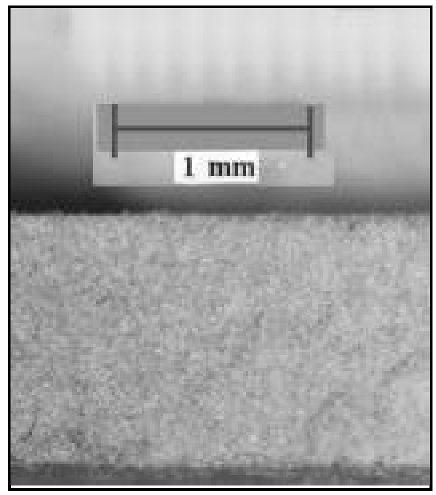

Figure 2. Photograph of the fracture surface of a green stainless steel sample, 0.052" thick, 0.001" layers.

Similar results have been achieved with a variety of ceramics and metals including alumina, zirconia, alumina/zirconia composites, silicon nitride, tungsten, and molybdenum. Debinding and sintering or HIPing of photoformed samples have resulted in high densities and strengths comparable to conventionally processed materials. Resultant microstructures are virtually identical to those made by conventional powder processing techniques. Further demonstration of the integrity of samples produced was the substantial ductility observed during flexure testing of the stainless steel samples and limited ductility observed in tungsten alloy (93W:4.9Ni:2.1Fe) specimens.

Table 1 summarizes published information on the resin characteristics and sintered strengths of these materials. Based on these initial, but broad results, it appears feasible to achieve desirable physical/mechanical properties in many ceramics and metals. This is a strong indication of the commercial potential of the technology; however other aspects must be considered, including dimensional accuracy and surface finish, component size and shape complexity capability and process economics.

Dimensional Accuracy/Surface Finish

The importance of achieving good dimensional accuracy is evidenced by the substantial broadening of end uses of stereolithography models (SLA models) over the last few years with the reduction of dimensional errors below 0.002" rms over the 9.5" x 9.5" *UserPart*.[6] As of this writing, very limited data on dimensional accuracy and surface roughness using highly filled ceramic and metal resins have been published, however, it can be reasonably assumed that the ultimate dimensional accuracy and surface finish achievable will not be as good as with conventional stereolithography, because of perturbations due to particulate fillers, but will be comparable to those achieved using conventional powder processing techniques.

Table 1. Resin characteristics and sintering results for a variety of materials made by stereolithography-fabrication

Material	Solids Loading (vol%)	Cure Depth (max)	Sintered Density	Flexure Strength (avg.)
Al_2O_3	55	>0.030"	>99%	360 MPa
ZrO_2 ¢	45	0.006"	>97%	530 MPa
Al_2O_3/ZrO_2	50	>0.020"	>99%	410 MPa
Si_3N_4*	55	0.004"	>98%	>1GPa
316L SS	55	0.003"	>95%	455 MPa
W alloy	55	0.002"	95 - 98%	>1GPa
Mo	50	0.002"	NA	NA

¢W.R. Grace and Co.
*SRI International and St. Gobain/Norton, HIPed Si_3N_4 (ref. 4)
All other data from Ceramic Composites, Inc.

Light scattering from ceramic or metal particles is not expected to contribute significantly to dimensional errors in green state components. Scattering should be quite uniform and predictable due to the high uniformity of the inks and the consistency/controllability of the building process. Line width compensations can be made similar to techniques developed for conventional stereolithography which should enable accurate dimensional control. Dimensional accuracy will ultimately be limited by the ability to control and predict sintering shrinkages, with the ability to achieve high solids loadings in the inks contributing significantly toward this objective. Using conventional processes such as dry powder pressing and sintering of ceramics, green densities of 50—60 vol% and as-sintered dimensional tolerances of ±0.003"/inch are typical.[7] In this uniaxial pressing method, slight variations in shrinkage are the result of green density variations which inevitably occur due to die wall friction and contribute to dimensional errors.

Stereolithography fabrication has some potential advantages here since green density uniformity is determined by the ink uniformity and the consistency of the building operation, both of which are quite good. Some variations may arise due to the laminar build structure and potential grain orienting effects (for non equiaxed particles) of the blade casting layer application method; however, manifestations of these potential sources have not yet been observed. It is difficult to predict what the ultimate dimensional accuracy of the direct process will be, although it will likely be better than the ±0.003"/inch of uniaxial pressing of dry powders, due to the expected better uniformity in green density, particularly in complex shapes. What is certain is that it will require a development effort similar to that put forth by 3D Systems and SLA users to improve the dimensional tolerance on the SLA *UserPart*.

Contribution to the surface roughness of sintered parts formed by stereolithography can be divided into two categories: 1) the effects of light scattering during part building; and 2) the effects related to powder processing which are common among many powder consolidation approaches.

Figure 3 shows the effects of light scattering on a ~45° surface of an alumina part built with an argon ion laser using CCI's alumina resin at 50 vol% solids loading. The layer thickness is 0.005" and peak to valley roughness resulting from light scattering is roughly 0.001" (~25 µm). Optical profilometry[8] on the edge of a vertical surface of the same part confirmed the peak to valley roughness to be in the range 0.001" - 0.0015" (25 - 35 µm).

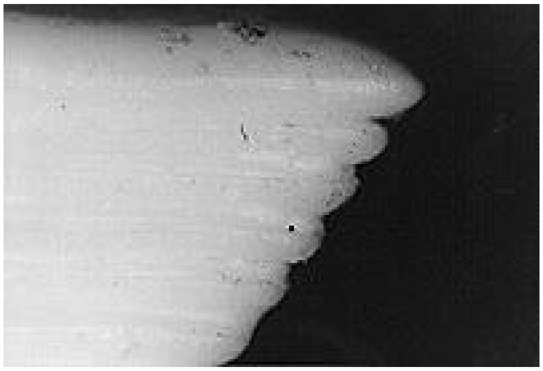

Figure 3. Edge scalloping effects resulting from light scattering in an alumina resin cured with an argon ion laser.

The source of the scalloping effect is depicted in Figure 4 which compares the cured line profile for a conventional SLA resin to that of a highly loaded alumina resin. In the unfilled resin, the profile is determined by the Gaussian shape laser beam and the absorption behavior of the resin as described in the Beer-Lambert Law.[i] In a filled resin, light at normal incidence to the resin surface is refracted and reflected as it encounters the higher refractive index alumina particles. This results in significant exposure at points laterally distant from the point of incidence. The result is broadening at the waist of the cured line profile and the edge scalloping effect seen in Figure 3. This scalloping effect is similar in scale to the stairstepping texture seen on contoured or angled surfaces in all rapid prototyped models. The degree of scalloping in other ceramic and metal filled resins has not yet been evaluated but is likely to be at least partially dependent on the optical properties of the inorganic particles.

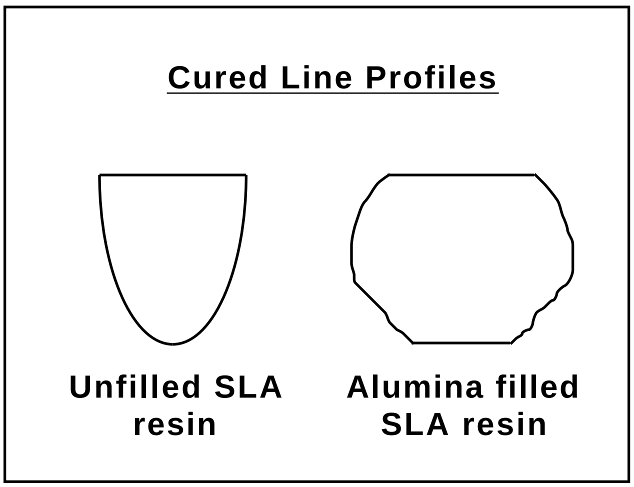

Figure 4. Cured line profiles for unfilled and filled resins.[3]

Optical profilometry on the top (up facing) surface of the part showed average roughness (Ra) values of ~1 µm. This roughness is primarily attributed to the second category of contributing factors, the effects of powder processing operations. In this category, surface pores, powder agglomerates, and miscellaneous debris contribute to high roughness values. In stereolithography processing, concerns over the presence of large agglomerates are reduced compared to some processes such as dry powder compaction in which spray dried powders are used to enhance flowability. However, other concerns may arise such as air bubbles generated during the recoating step or cured resin debris which may have broken off from neighboring parts. Thermal debinding can also contribute surface roughness in the way of small blisters or pin holes if not carefully controlled. These factors can contribute roughness features that are tens of microns to hundreds of microns, but are manageable with careful process development and control.

On a finer scale, grain boundary grooving and grain surface faceting on sintered surfaces contribute to roughness at the scale of fractions of the materials grain size. These effects can be partially controlled by minimizing grain growth during sintering, but for the most part sintering schedules are optimized based on desired mechanical properties and the resulting roughness is removed using various finishing steps. For ceramics, these effects are typically very small, of the order of tenths of microns to a few microns. For metals, which typically have larger grain sizes, these factors could be significant, of the order of a few to tens of microns. When lower roughness is required, finishing operations are used including fine grinding and various polishing techniques. Finishing operations are common for most ceramic and many metal forming processes including metal casting, forging and extruding as well as most stereolithography produced models, the latter to remove or lessen the stairstepping texture which results on contoured or angled surfaces. Table 2[10] shows how the stairstepping effect scales with layer thickness on a 45° surface and compares the calculated roughness to some common fabrication processes.

Table 2. Typical Surface Roughness of Fabrication Processes (ref. 10)

Fabrication Process	Arithmetic Average Surface Roughness (µm)
Precision Finish Grinding	0.1 - 0.2
Roller Burnishing	0.2 - 0.4
Milling (carbide cutters)	0.4 - 0.8
Die Casting	0.5 - 3.8
Finish Turning	0.8 - 3.2
Rough Turning	13 - 26
Cutting Torch Chip and Saw	13 - 51
Stereolithography (45° surface)	
250 µm layer	44
100 µm layer	18
50 µm layer	9

Note that scalloped edge roughness resulting from light scattering in filled resins is similar in size to the roughness resulting from the stairstepping texture on a 45° surface.

Process Economics

One of the most important parameters to evaluate when assessing the commercial potential of a new fabrication approach is the process economics relative to existing approaches. For direct stereolithography of ceramics and metals the task is complicated by the flexibility of the new process and the wide variety of existing forming operations with which to compare. A case by case approach is warranted, but not time efficient. Instead a number of representative parts have been designed which span a wide range of component sizes and geometric complexities. The representative parts were sent out to industry for bid. Detailed cost estimates based on direct stereolithography fabrication were prepared and compared to the quotes from industry. From these representative cases trends can be extracted which will help steer development towards applications with the highest payoffs.

The first two case studies are reported here. Both are relatively small parts; the cylindrical connector (Figure 5) is 0.5" in largest dimension and the block connector (Figure 6) is ~1" in largest dimension. The cylindrical connector is geometrically simpler and axially symmetric. The block connector is slightly more complex and axially asymmetric. Since alumina ceramic resins appear to be substantially compatible with current stereolithography machines, a fine grained, high purity alumina material was specified and quantities of 80, 500 and 1,000 were requested.

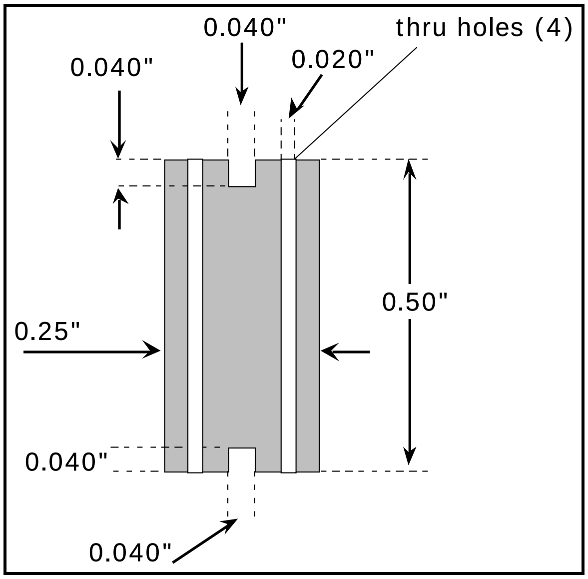

Figure 5. Cylindrical connector

Stereolithography estimates were prepared using SLA 250 and SLA 500 machine costs and build parameters. The following processing steps were considered for the cost estimates:

1) Resin materials and preparation
   — powder preparation (alumina costs, processing labor)
   — resin preparation (organics costs, labor)
2) Green part fabrication
   — part building (machine time)
   — part cleaning (labor)
3) Thermal processing
   — debinding and sintering (labor)
   — quality control (labor)

Note that all labor costs are based on loaded rates using overheads typical of small to medium size ceramic manufacturing businesses.

Resin materials and preparation consists of two cost components, the first is powder preparation including alumina costs @ $1.50/lb ($0.013/cc) and technician labor to mill and sieve the powder to eliminate large agglomerates and debris. The second component is the resin materials and preparation costs and includes the organic constituents (monomers, dispersants and photoinitiators) and the technician labor to prepare and tend the formulation. Pot losses of 10% were included for each transfer of material from one container to another. Resin Costs = $0.038/cc. To estimate the resin costs per part, the part volume was estimated based on the green part height times the green part's largest cross sectional area. This accounts for resin losses incurred during part washing. The estimated volume of the cylindrical connectors is 0.786cc and the block connector is 9.51cc.

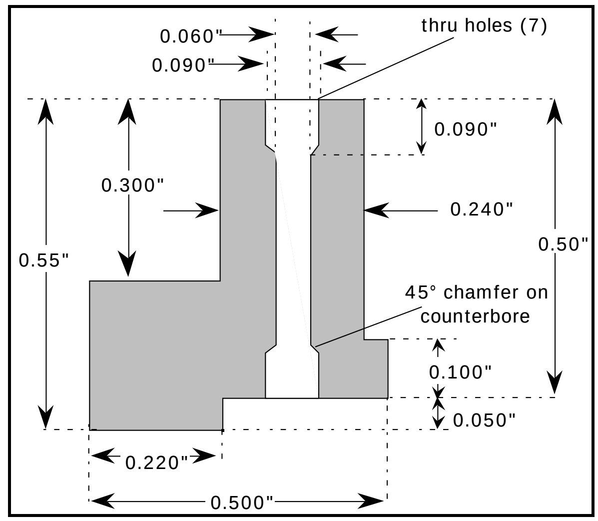

Figure 6. Block connector.

Resin Cost per Part

Cylindrical Connector	Block Connector
$0.033/part	$0.40/part

Green part fabrication consists of part building on an SLA machine and part cleaning. Part building estimates were made for a SLA 250 machine utilizing a 40 mW HeCd laser and two vat sizes; 6" × 6" × 2" and 10" × 10" × 2". SLA 500 machine estimates were based on a 200 mW Ar+ laser and three different vat sizes 6" × 6" × 2", 10" × 10" × 2" and 20" × 20" × 2". Discussions with several SLA services bureaus verified average machine time costs at $75/hour for SLA 250 and $125/hour for SLA 500 machine time.

Build time was estimated by considering the laser scan rate required to provide secure interlayer bonding using layers 0.005" thick. The time to scan an entire layer was calculated based on this rate and the estimated recoating times for the different vat sizes was added to give the total layer build time. The number of layers per part was calculated based on oversized part dimensions which took into account 20% linear shrinkage during sintering (actual shrinkage is closer to 15% for loadings > 50 vol%). The total build time for one batch of parts was calculated and a build cost/part was produced given the number of parts per batch and the machine time hourly rates. The following parameters were used:

Energy dose to build using 0.005" layers	60 mW/cm^2
HeCd laser scan rate (26 mW/cm^2 at resin)	230 mm/s
Ar+ laser scan rate (200 mW/cm^2 at resin)	1780 mm/s
Recoating time, 6" × 6" vat	0.5 min.
Recoating time 10" × 10" vat	1.0 min.
Recoating time 20" × 20" vat	1.5 min.
# of cylindrical connectors per batch	
6" × 6" vat	196
10" 10" vat	576
20" × 20" vat	2304
# of block connector parts per batch	
6" × 6" vat	32
10" 10" vat	80
20" × 20" vat	351

Part clean up time including removal from the vat, batch washing in solvent and individual spray cleaning, drying and inspection was estimated and added to the machine time costs to give a cost/part for green part fabrication. Table 3 shows these estimates.

Table 3. Green part fabrication costs/part

	Ar+ laser		HeCd laser	
Vat	Cylindrical	Block	Cylindrical	Block
6 × 6	$2.63	$14.39	$7.14	$44.87
10 × 10	$2.25	$10.88	$6.60	$37.24
20 × 20	$1.93	$9.19	-------	-------

Thermal processing costs were estimated for a relatively small furnace in which both debinding and sintering can be performed. The thermal processing cost estimates are based on labor to set up and take down the parts and kiln furniture. Labor time was estimated assuming the furnace is run fully loaded. Based on the hot zone volume of the furnace, the furnace batch size for cylindrical connectors is 630, and for the block connectors is 160.

Thermal Processing Costs per Part
Cylindrical Connector = $0.48/part
Block Connector = $1.86/part

The total costs/part for the three different vat sizes that could be used and the two different laser systems are given in Table 4.

Table 4. Total costs/part for stereolithography fabrication of the cylindrical connector and the block connector.

	Ar+ laser		HeCd laser	
Vat	Cylindrical	Block	Cylindrical	Block
6 × 6	$3.14	$16.65	$7.65	$47.13
10 × 10	$2.76	$13.14	$7.11	$39.50
20 × 20	$2.44	$11.45	-------	-------

An important factor not included in these estimates is the yield. Yields for direct stereolithography fabrication of ceramics have not been studied, but given the consistency of the build operations and the mature state of thermal processing of ceramics yields comparable to existing powder processing methods are expected.

Table 5 summarizes the quote received for the two parts. The cylindrical connector quote was based on using an extrusion process and green machining to cut the end grooves. To fabricate the block connector the vendor selected a dry powder pressing approach. The yields assumed by the vendor are not known and could be a significant factor in the costs. Yields for stereolithography fabrication are not presently known and it is likely that yields will be low initially and improve as process development progresses. Yield was not considered in this cost analysis.

Table 5. Quotes received from ceramic vendor for fabrication of alumina connector parts.

Part/Qty	price/part	tooling cost	Total price/part
Cyl/80	$21.38	$1200	$36.38
Cyl/500	$11.05	$1200	$13.45
Cyl/1000	$10.11	$1200	$11.31
Block/80	$31.18	$4200	$83.68
Block/500	$13.54	$4200	$21.94
Block/1000	$11.86	$4200	$16.06

In comparing these quoted costs with the estimated stereolithography costs some trends can be seen. As expected, for smaller lot sizes the tooling costs per part dominate the quoted prices and stereolithography estimates are substantially lower, 80–90% lower for the cylindrical connectors and 45–80% lower for the block connectors depending on the laser used. Stereolithography maintains a significant cost advantage over the extrusion process for the smaller cylindrical component, even at high volumes. For a quantity of 1,000 parts the cylindrical connector has a 40–75% lower cost depending on the laser used. Stereolithography fabrication using the lower power and slower HeCd laser loses its cost advantage for producing the larger block connector at moderate quantities–for 500 parts the dry powder pressing method is ~65% lower cost. However, stereolithography using the higher power Ar+ laser maintains a ~30% cost advantage over dry powder pressing for quantities of 1,000 and higher.

Estimated delivery times for stereolithography fabrication are based on part build and cleaning times and thermal processing times including furnace set up and tear down. For a quantity of 80 parts the estimated delivery time is the same for both parts—5 days. For a quantity of 500 parts the estimated delivery time for the cylindrical connectors is 5–7 days depending on the laser system used. Fabrication of 500 and 1,000 block connectors the Ar+ laser system would be used and a larger furnace would be required so that the lot could be thermally processed in one or two runs. Scaling up to the appropriate size equipment enables delivery times of 6—12 days. Fabrication of 1,000 cylindrical connectors would also require an appropriately sized furnace and a delivery time of 5 days is expected.

In comparison, the delivery time for the quoted specimens is 12 weeks for all quantities, indicating that the tooling lead time is a primary factor.

Conclusions

Stereolithography fabrication of ceramic and metal components appears to be a commercially viable process offering significantly reduced costs and lead times, although substantial development is needed. This initial analysis indicates that stereolithography has the greatest economic advantage for small complex shape parts produced in low volumes, although in many cases the economic advantages carry through to larger component sizes and larger volumes. Further development will provide information on stereolithography yields, a potentially major factor not included in this analysis. The feasibility of producing ceramic and metal components with microstructures and mechanical properties similar to conventionally processed materials has been demonstrated. Dimensional accuracy is expected to be comparable to powder processed ceramics and metals, however surface roughness due to stairstepping and light scattering is expected to be slightly higher in stereolithography produced parts.

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