Metal and Ceramic Components made via CAM-LEM Technology

Z. E. Liu, P. Wei, B. Kernan, A. H. Heuer, and J. D. Cawley
Department of Materials Science and Engineering
Case Western Reserve University, Cleveland OH

Abstract - CAM-LEM (Computer-Aided Manufacturing of Laminated Engineering Materials) is an SFF technology suitable for many engineering materials for which feedstock is available in sheet form; lamination and post-processing procedures are materials specific. Two methods for producing sheetstock, tapecasting and compression molding , are discussed and contrasted. Ceramic and metallic components that have been produced via CAM-LEM are described.

1. Overview of Process - Computer-aided manufacture of laminated engineering materials (CAM-LEM) is a sheet-feedstock-based process for rapid prototyping capable of producing functional components directly using engineering materials (advanced ceramics, metals, or engineering polymers). An outline of the process is given in a companion paper [1] and prior publications [2-4]. A significant unique feature to CAM-LEM is that it is a "cut-then-stack" approach in which the production of pseudo-2D contours via laser cutting and stacking are carried out as separate operations. This approach required the development of an automated process for precise manipulation of cut sheet stock [2], but offers three basic advantages. First, because each sheet is manipulated independently, it is possible to incline the feedstock during laser cutting so that the "tangent cutting" can be used to improve surface finish or increase build rate [1]. Secondly, as solid sheets are used, CAM-LEM offers a great deal of flexibility in the choice of materials that can be employed. Many materials are commercially available as sheets and essentially all powders can be pre-processed (in most cases, using a binder system) to produce sheet stock of a microstructure optimized for post-assembly thermal processing. Of particular interest for the production of ceramic and metal components, the use of a separate pre-processing step to produce sheet feedstock allows the use of very fine powders when desired without the typical flowability issues arising. Thirdly, because cut outlines are added sequentially, it is possible to build using a variety of feedstocks and to produce green assemblies that have spatially varying composition both from layer-to-layer and within a given layer.

The issue of tangent cutting is discussed elsewhere [1]. The following will address: the characteristics of feedstock suitable for CAM-LEM processing; the processes used for fabricating sheetstock; lamination; resultant microstructures within fired components; and typical components.

2. Sheet Feedstocks - The focus of this discussion is powder-based sheetstock, of which there are two classes that exhibit different characteristic behavior. The first is produced by tape casting [5]. Green tape produced by this method has roughly 55 vol. % inorganic powder, 15% organic binder, and the balance porosity. The porosity is typically finely divided, but continuous. The binder is typically linear, glassy and soluble in relatively benign solvents. Two types of alumina tapes have been used in CAM-LEM experiments; one cast from a nonaqueous suspension in a solution of polyvinyl butryal and the other cast from a suspension in a water-based acrylic emulsion. Such tapes are characterized by a high compressibility, low stiffness, and (depending on the glass transition temperature of the binder) a susceptibility to viscous flow under low loads. Both commercial tapes (Coors Electronic Materials, Chattanooga TN) and CWRU-produced tapes were used. For components built from these tapes, binder removal was effected through pyrolysis. The polymer was thermally decomposed volumetrically through controlled heating. The presence of continuous porosity allows gaseous decomposition products to be vented, minimizing the build-up of internal pressures.

The other class of tape is produced by compression molding or extrusion. In all the experiments described, sheet stock was fabricated by compression molding of a commercial granulated injection-molding feedstock (BASF, Wyandotte MI) [6]. In contrast to the tape-cast material, such feedstock contains virtually no porosity. Depending on the shape, size and size distribution of the inorganic powder, the feedstock has a solids loading of between 45 and 65 vol. %. The binder system has two components, the major phase being polyoxymethylene (POM) which is highly crystalline, nonpolar, and insoluble in most solvents. The sheetstock is strong, stiff, and of low compressibility. Due to its nonporous nature, binder removal is accomplished using a catalytic process. In the presence of gaseous nitric acid, POM depolymerizes at a temperature substantially below its melting point. Thus, the system is phenomenologically a "shrinking core" process; the polymer decomposes at the receding surface and the resultant gases are vented through the porous shell. Within the core, the polymer remains a crystalline solid.

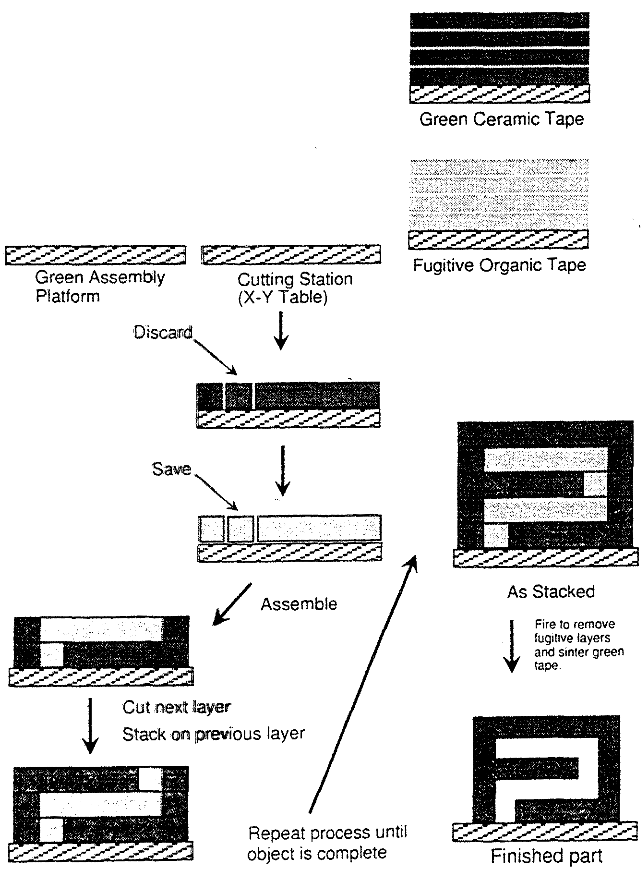

Figure 1. Schematic representaion of the use of two feedstocks in CAM-LEM.

As illustrated in Fig. 1, by using a cut-then-stack approach CAM-LEM offers the opportunity to build individual layers of two different types of materials, one of which can serve as a "fugitive," i.e., it can provide for temporary support during build, but is removed after lamination is complete, but prior to final densification. Beyond their use as temporary supports, such fugitives can serve as a pressure-transmitting medium during lamination, allowing a component of complex geometry to present a simple external shape after assembly. Two types of materials have been used as fugitives, one for each class of sheetstock.

For tape-cast sheetstock, the fugitive was also tape cast. The binders, solvents and procedure were essentially unchanged, but the filler was different. Rather than using a finely divided (≈0.5 μm) sinterable alumina, a coarse alumina (≈10-15 μm) mixed with low-ash corn starch was used. Upon heating to inter -

mediate temperature, the base material (fine alumina) developed modest strength prior to densification, whereas the fugitive tape was converted to a loose flowable powder that was easily removed.

The fugitive for the compression molded sheetstock was a commercial POM polymer sheet. During catalytic debinding, the polymer sheet decomposed, the small residue left behind during debinding being removed by pyrolysis during the initial stage of the sintering heat treatment.

3. Laser Cutting Behavior - Laser cutting is a complex function of laser beam intensity, table velocity, thermal properties of the green tape, tape porosity, and binder chemistry. As currently implemented, the laser cutting system employs a gas jet that is coaxial to the laser beam and which impinges directly on the sheetstock. Good laser cutting is associated with high absorption of laser light, low thermal conductivity of the tape, and temperature-independent high stiffness. Most materials give good cutting behavior. The only materials that have proven difficult to cut with a low power CO_2 laser are those that are of low absorption and which exhibit a broad softening range, e.g., nylon and polyethylene.

The characteristics of the laser-cut edge differ depending on the nature of the sheetstock. Some degree of taper is associated with all laser cutting. For tape-cast sheetstock, taper angles were on the order of 7-8°, whereas for the compression molded sheetstock, taper was roughly one-half, ≈4°. There was evidence of a heat-affected zone in the tape-cast alumina sheetstock; an approximately 50 μm thick dense skin at the laser-cut edge. In contrast, for the dense POM powdered metal tape, there was no observable change in microstructure right up to the laser cut edge. There are at least two plausible origins of the dense skin associated with laser cutting tape-cast sheetstock, localized melting and resolidification or viscous flow of the porous polymeric binder in the heat-affected zone. The second appears more likely, as stringer formation and beading were both found when laser cutting polymeric sheet that had a tendency to melt. The consequence of the densified layer on final microstructure after sintering remains an area of research activity.

4. Lamination Methodology and Firing Schedules - Very different techniques were used to laminate the tape-cast PVB sheetstock and the compression-molded POM sheetstock.

4.1 Solvent-Based Method of Tacking and Lamination of Tape-Cast PVB Alumina Tape - The use of solvents to soften the surface of the interface of mating tapes and aid in lamination is not a new idea, but conventional practice, for example, in the fabrication of multilayer ceramic substrates typically involves large strains (>10%) and are not suitable for lamination of green stacks when it is necessary to preserve precise external dimensions. The advantage of solvent lamination over thermocompression is that only the near-surface region of the tapes is softened, so that deformation is localized.

4.1.1 Adhesive Formulation - In these studies, an ethanol/toluene mixture was applied between sheets during stacking. The resultant tacky surfaces ensured that successive sheets were immobilized as they were added to the stack. The volatile nature of pure ethanol and toluene, coupled with capillary suction into the porous green tape, it caused difficulty in depositing and maintaining a uniform film of solvent. Evaporation was suppressed and the viscosity increased through the addition of polypropylene glycol (1000 m.w.) to form an adhesive solution that rendered surfaces persistently tacky. In most experiments, a triaxial formulation consisting of 40 wt.% ethanol, 20 wt % toluene and 40 wt.% polypropylene glycol was used. Both solvents were removed by vapor phase transport through the porous tape during drying. Polypropylene glycol is a plasticizer for PVB and is presumed to migrate away from the interface during the initial stage of firing, either by capillary action into the pore space and/or by dissolution into the binder.

4.1.2 The Lamination Process - Figure 2 schematically outlines the steps of the adhesive lamination process which was developed for CAM-LEM technology. Using this process, 30 layer samples consisting of 25.4 mm square sheets were stacked and laminated. [In these experiments manual, rather than robotic, stacking was used for experimental convenience.] In the first step, a layer of tape was placed on a smooth, glass plate and brushed to remove cutting debris. Once the surface was clean, adhesive was uniformly applied to the entire surface with an atomizer (approximately 3 x 10^{-4} gm/mm^2). The next layer of tape was added to the stack and rolled with a 0.45 kg, finely polished, aluminum roller (50.8 mm diameter). Rolling was initiated at the center of each layer, followed by 5 complete strokes traversing the entire surface of the slice. This process was repeated for each additional layer. On completion of the stack, samples were vacuum-degassed, by placing the rolled stack in a latex bag and evacuating (using shop vacuum) with a micro-pipette and holding for 30 minutes. After evacuation, the sample was sealed within the bag, uniaxially pressed at room temperature to 1 MPa and held for 10 seconds. The sample was removed from the bag, dried, and fired. Samples were debinded by heating at 0.2 °C/min. to 800°C, and then more rapidly heating at 3 °C/min to 1560°C for sintering. Dimensional changes were measured after each stage with a micrometer, and all samples were sectioned after sintering. Die penetrant was used to aid in delamination and crack detection.

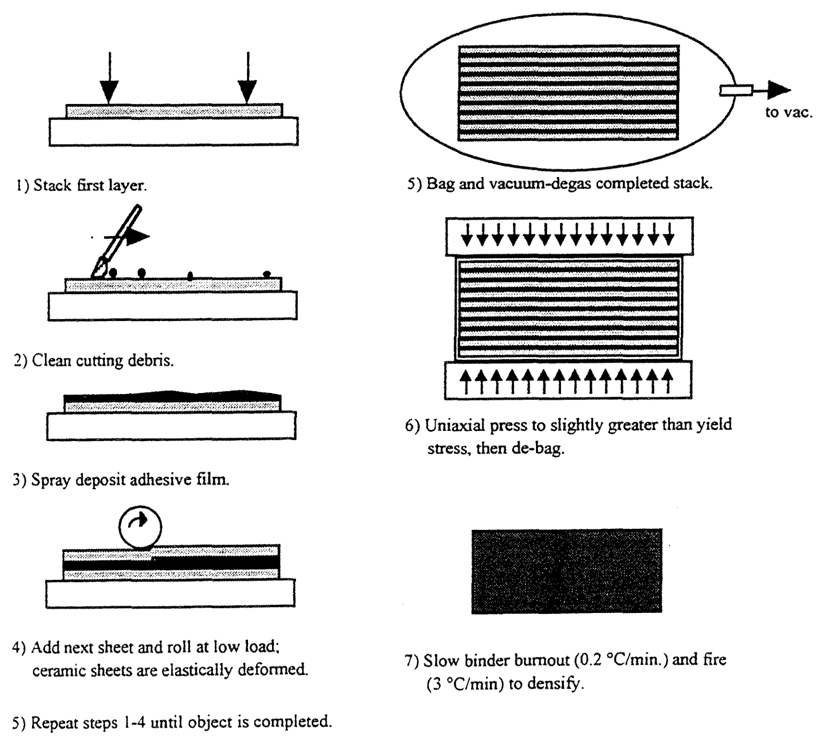

Figure 2. Schematic of the adhesive lamination process.

Thirty-layer samples were used to test the adhesive lamination process. In all samples made to date, the 30 layers completely fused together and no lamination seams were detected; in marked contrast to the high density of lamination defects observed using other techniques, such as warm isostatic pressing. The rolling load was very small (< 0.45 kg.) and the applied stress was only one-half of the yield stress for the tape. No dimensional changes could be detected in the green state after rolling. The function of the roller is to ensure conformation of each tape to the underlying stack, and to express both bubbles and excess fluid, so that a thin uniform layer of the adhesive solution is left at each interface. The vacuum degassing step was included to assist in the removal of bubbles and excess fluid, but it was subsequently determined to be unnecessary. It is during the uniaxial pressing step that yielding occurred, but, even during this step, dimensional changes were small, $\leq 0.5\%$ linear change. All samples demonstrated linear shrinkages of ≈ 15 % during sintering, which is typical for these tapes.

4.1.3 Fugitive Tapes - The adhesive lamination process requires that the applied load, during uniaxial pressing, be effectively transmitted throughout the entire stack, so that all interfaces are approximately equally loaded. Thus, it is highly desirable to prepare a fugitive that has a mechanical response similar to that of the baseline tape, particularly at small strains. The need to match mechanical properties proved to be the key criterion for a successful fugitive. This is demonstrated in Figs. 3-5.

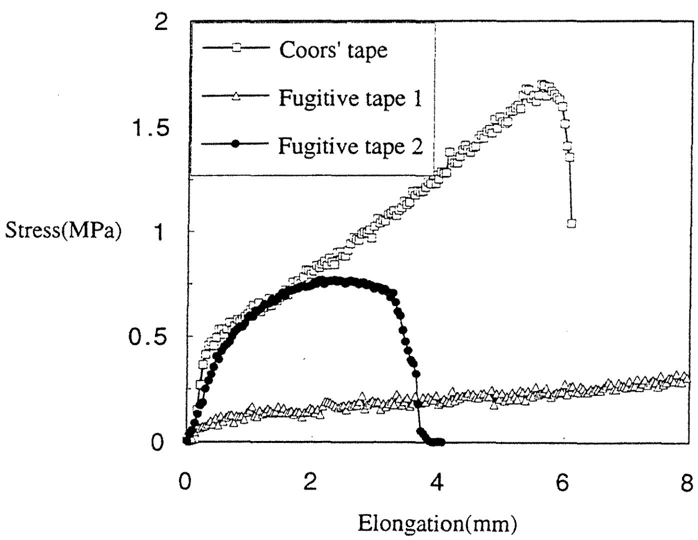

Figure 3. Mechanical behavior of two fugitives compared to the baseline alumina tape.

Figure 3 shows stress-strain curves from tensile tests of two fugitive tapes (prepared with small filler, but different binders) compared to that for the baseline PVB alumina sheetstock. Fugitive-1 is of lower stiffness and yields at a significantly lower stress than the baseline material. Although Fugitive-2 also deviated from the baseline at large strains, its behavior reasonably approximates that of the baseline material at small strain. The consequence of this on lamination behavior is readily seen in the simple, but asymmetric, specimens shown in Fig. 4 and 5. Specimens were prepared using each of the fugitives, laminated, fired, sectioned, and examined with the aid of a die penetrant. As evident in Fig. 4, the softer fugitive was ineffective as a pressure transmitting medium so that lamination defects were present in the final piece. The fugitive designed to match the base line material was completely successful and the microstructure of the finished piece is devoid of lamination defects, Fig. 5.

4.2 Thermocompressive Lamination of POM Powdered-Metal Tape - Because the compression molded POM tapes are nonporous and the polymer is insoluble, adhesive lamination cannot be used with this type of sheetstock and thermocompression was needed. Initial experiments attempted uniaxial forging at modestly elevated temperatures. However,

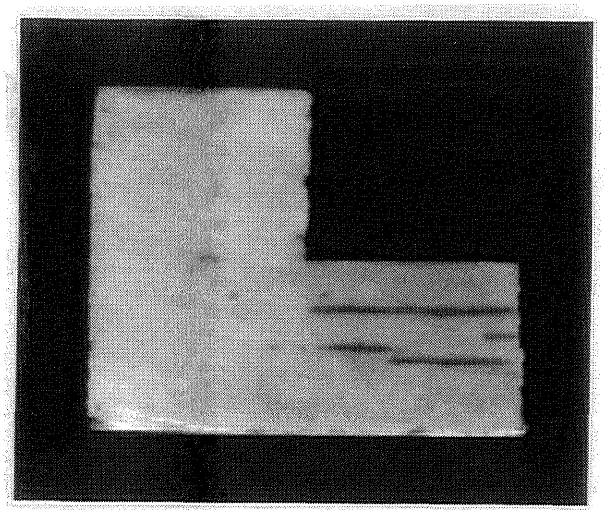

Figure 4. Cross section of a sample laminated with fugitive-1. Note the delamination revealed by die penetrant.

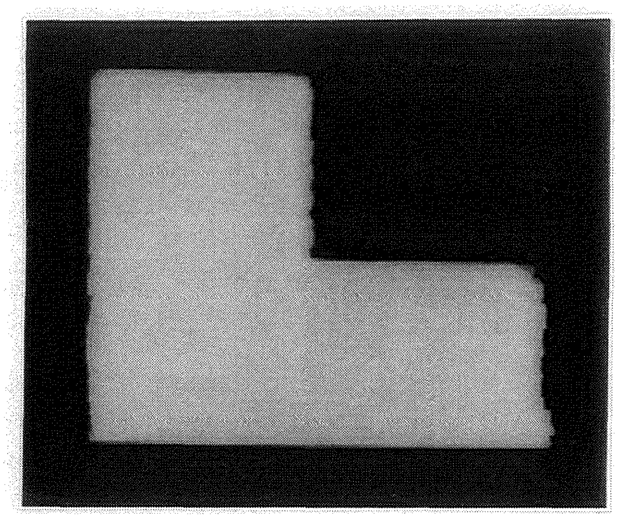

Figure 5. Optical micrograph of a sample laminated with fugitive-2, in which there was no delamination.

control proved difficult, as the polymer remained stiff and unyielding over a wide range in temperature, but then suddenly became fluid and susceptible to gross deformation. A system was needed that would provide both a confining pressure and accommodate a variety of shapes.

The procedure adopted, "quasi-isostatic pressing," involves burying the piece in a low friction powder (120 μm spherical graphite granules) within the cavity of a large diameter (relative to the piece dimension) uniaxial press. The temperature is raised and a load applied to the rams. With the powder as a pressure transmitting medium, the applied load on the piece is anisotropic; the load parallel to the pressing direction is roughly twice that perpendicular to the pressing direction [7].

This method is very effective at achieving 100% lamination efficiency. Backing plates were sometimes necessary to preserve flatness and, in some instances, surface texture developed during pressing. The primary issue for such lamination is the absence of an adhesive to tack sheets together during stacking. In these experiments, registration of the individual cut sheets was achieved through the use of fugitive pins machined from a block of commercial POM. In addition, the selective application of a water-soluble glue (polyethylene oxide) to the exterior surface during building was used.

5. Catalog of CAM-LEM Parts - Although a wide variety of sheetstocks are compatible with CAM-LEM technology[2], including a wide variety of green ceramic tapes (e.g., silicon nitride, PLZT, and zirconia), the primary material that has been used to date is a commercial high-alumina material. Figure 6 is a catalog of photographs of some of the alumina pieces that have been produced. Each of these pieces was chosen to test a particular feature of the CAM-LEM process. The ceramic head (CAD file downloaded from the internet) demonstrates the ability to manufacture relatively large blocky components which require large areas of lamination and have a large characteristic distance for binder burnout. The amphitheater flange (CAD file created in AutoCAD™) demonstrates the ability to preserve flatness across wide spans and to process components with both thick and thin walled sections. The dogbone test specimen (CAD file created in AutoCAD™) illustrated the ability to produce both test specimens and actual components using the same process, so that material property data can be collected on material of equivalent microstructure to that which will be put in service. The section of a dog femur, the ceramic turbine blade and the channel plate all illustrate the ability to produce hollow shapes that are difficult to produce using hard tooling. The dog femur (CAD file derived from computed tomography scan of an actual bone) has an irregular interior cavity from which it would be difficult to extract an insert after forming. The section of a ceramic turbine blade (CAD file modified in Pro/Engineer™) shows a regular shape that is equally difficult to produce, in this case because of the twist of the interior voids.

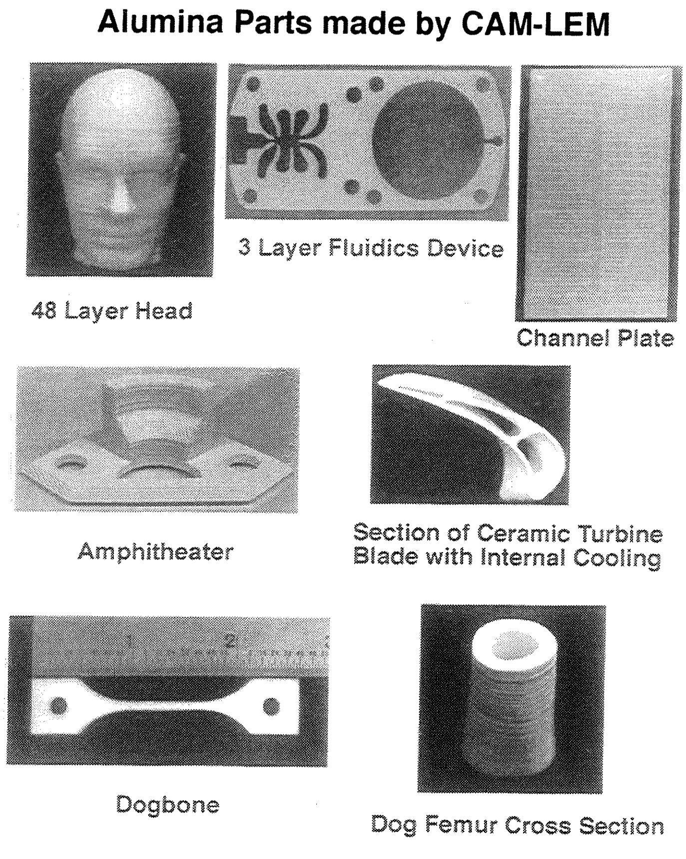

Figure 6. Catalog of ceramic CAM-LEM parts.

The channel plate is actually a three-layer structure, the serpentine structure is a ≈2 m. long capillary channel and it is sandwiched between dense plates that have small holes (0.5 mm dia.) that serve as an inlet and outlet. The fluidics device (CAD files modified in AutoCAD™) is a ceramic prototype of a production component that was manufactured to tolerance and performance tested by the manufacturer of the metallic equivalent.

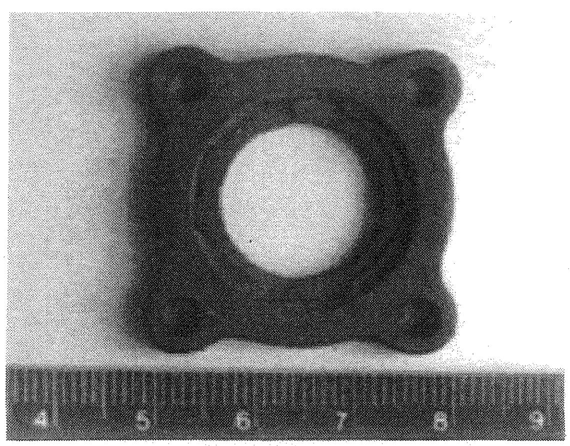

Figure 7. Stainless steel made by CAM-LEM.

Figure 7 show a metallic thrust plate that was fabricated from 316L stainless steel. The CAD file was generated in Pro/Engineer™ using a blueprint that was supplied. The sheetstock was compression-molded tape made from commercial feedstock. This piece demonstrates that components can readily be made using a sheetstock that is nonporous and stiff. Also of significance is the demonstration that conventional POM polymer sheet can be used as a fugitive phase; they are of adequate stiffness and can be readily removed during catalytic debinding.

6. Summary - Two classes of sheetstock have been produced that are compatible with CAM-LEM technology for the production of engineering. Each type of sheetstock can be used to produce both engineered ceramic and metallic components. Different lamination methodologies have been developed for each class of feedstock. An array of components have been produced in alumina, and a limited set has been produced in stainless steel.

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References

[1] Y. Zheng, S. Choi, B. Mathewson, and W. Newman, "Progress in Computer-Aided Manufacturing of Laminated Engineering Materials Utilizing Thick, Tangent-Cut Layers," these proceedings.

[2] B. B. Mathewson, W. S. Newman, A. H. Heuer, and J. D. Cawley, "Automated Fabrication of Ceramic Components from Tape-Cast Ceramic," p. 253 in *Solid Freeform Symposium Proceedings*, University of Texas at Austin Publishers, Austin TX, 1995.

[3] J. D. Cawley, Z. Liu, W. S. Newman, B. B. Mathewson, and A. H. Heuer, "Al_2O_3 Ceramics Made by CAM-LEM Technology," p. 9 in *Solid Freeform Symposium Proceedings*, University of Texas at Austin Publishers, Austin TX, 1995.

[4] J. D. Cawley, A. H. Heuer, W. S. Newman, and B. B. Mathewson, "Computer-Aided Manufacturing of Laminated Engineering Materials," *Am. Ceram. Soc. Bull.*, 75 [5] 75 (1996).

[5] R. E. Mistler, "Tape Casting: The Basic Process for Meeting the Needs of the Electronics Industry," *Am. Ceram. Soc. Bull.*, 69 [6] 1022 (1990).

[6] J. Ebenhöch, "Injection Molding of Hardmetals Using a Polyacetal Based Binder System," p. 261 in *Advances in Particulate Materials, vol. 4: Metal and Ceramic Injection Molding* Metal Powder Industries Federation, Princeton NJ, 1994.

[7] W. M. Goldberger, "Electroconsolidation Rapidly Densifies Powder Preforms," Adv. Mater. Proc. 141 [6] 43 (1992).