Automated Fabrication of Monolithic and Ceramic Matrix Composites via Laminated Object Manufacturing (LOM)

Don Klosterman, Richard Chartoff
Nora Osborne, George Graves
Rapid Prototype Development Laboratory and
Ohio Rapid Prototype Process Development Consortium
University of Dayton
300 College Park
Dayton, OH 45469-0130

Abstract

This report summarizes recent developments in a research program for fabricating advanced monolithic and ceramic matrix composite parts using Laminated Object Manufacturing (LOM). Both silicon carbide (SiC) and SiC/SiC composites are discussed. The LOM process is used to produce green forms that are then densified using various post processing operations. The monolithic ceramic LOM process was advanced through the implementation of an automated solvent spray bonding step, significant improvement in decubing with new software, and an intensive round of mechanical characterization. The LOM process for making CMC green forms is fully developed. This entailed implementing a process for making suitable SiC fiber preforms, a laser cutting capability, a decubing strategy, and a binder resin cure procedure. Further research is ongoing for the post processing pyrolysis and reaction bonding steps as discussed herein.

Introduction

The rapid prototyping and manufacturing of monolithic ceramics and ceramic matrix composites (CMCs) is being studied by a university/industry collaborative team lead by the University of Dayton and Helisys, Inc. This technology, based on Laminated Object Manufacturing (LOM), will be capable of producing high performance, near-net-shape structural ceramic parts. The standard LOM process [1] is illustrated in Figure 1. The technical objectives of the program are: 1) to produce CMC parts with structural integrity similar to CMC parts made by current fabrication techniques, and 2) to develop a commercially viable machine capable of automated fabrication. The rationale for using this process for composite fabrication is LOM's inherent capacity to handle flat sheet materials, to produce geometrically complex objects, and to operate with a high degree of automation, all without special tooling or fixturing.

The program involves a multidisciplinary effort that can be decomposed into the following interrelated sub activities:

- Machine design and control
- Software modifications and enhancements
- Ceramic preform formulation and manufacture
- Ceramic LOM process development
- Laser cutting
- Binder burnout
- Ceramic precursor pyrolysis
- Ceramic densification via reaction bonding
- Mechanical testing and characterization
- Part building and demonstration

Past efforts in all of these areas have been summarized in previous articles [2-6]. In this paper, recent progress in the areas of ceramic preform formulation and manufacture, ceramic LOM process development, ceramic precursor pyrolysis, and mechanical testing and characterization will be presented.

Monolithic Ceramics

<u>Automation of Solvent Spray</u>

The LOM process for monolithic ceramics is being developed using SiC as a focus material system. Ceramic tapes of 250 μm thickness comprised of a bimodal SiC powder (3 μm and 60 μm), carbon and graphite powders, and a polymeric binder system are fabricated with a standard doctor blade tape casting process. As described in previous reports [3], the tapes are laminated on a standard LOM2030 using a solvent assist spray technique. A hobby/artist's airbrush is used to apply a fine spray of butanol to the resin rich side (bottom) of the ceramic tape. The solvent acts as a tackifier to enhance the strength of the lamination, lower the required lamination temperature, and drastically increase the reliability of repetitive layer lamination, all compared to lamination without using a solvent. Butanol as a solvent has several advantages: low vapor pressure so that it doesn't evaporate during the spraying operation, reduced toxicity compared to aromatic solvents, and reduced flammability compared to lighter solvents.

A semi-automatic spraying process was developed to facilitate efficient, reliable, and reproducible part building (see Figure 2). The airbrush nozzle was mounted to the laser gantry of a LOM1015 machine. Solvent was fed to the nozzle through a flexible tube connected to a reservoir. The spray stream, directed normal toward the platform, was manually turned on and off with a solenoid switch regulating the gas pressure. A standard LOM software routine (i.e., "Cut Tiles") was used to move the nozzle in a raster pattern while the solvent spray was activated. Tapes were placed and removed manually from the platform. The sprayed tapes were placed solvent side down on the part being built on an adjacent LOM2030.

The following parameters affect the solvent spray process: internal nozzle adjustments, gas pressure, gantry speed, platform to nozzle distance, raster spacing, overall area sprayed. All these were determined by trial and error within a day's time, and they remain the same for all parts with the exception of the overall sprayed area. This procedure has proven itself effective: parts of up to 50 layers have been built in an efficient, methodical, and reliable manner without any lamination flaws. Although this process is only semi-automatic, personnel with minimal training can easily handle it. Only one person is required to run the process.

Decubing

The application of solvent to improve layer adhesion has important implications on the decubing step. The solvent assists in partially fusing the layers together, thus blurring the boundary. In general, the ease of decubing relies on the existence of an interface which, regardless of whether it is strong or weak, *must be distinct*. After building several different ceramic parts with various geometries, it became apparent that the decubing step was difficult and tedious at best, and in many cases ceramic parts could not be decubed without severe damage. To address the problems of decubing ease and damage, two strategies were investigated: adaptive crosshatching and adaptive surface burnishing. Both these strategies are similar and required additional software to be developed. These strategies, illustrated in Figure 3, involve selectively modifying the region of overlap between cube area and part area in successive layers. In the case of adaptive crosshatching, the area is cut with a fine (0.5 mm) crosshatch. With adaptive surface burnishing, the surface of the overlap zone is burnished with the laser, removing the binder from the surface while leaving the powder. The thin layers of loose powder serve as a release mechanism during decubing.

Software developed by Helisys, Inc. for adaptive crosshatching was tested on three parts shown in Figure 4. This strategy was largely successful. Each part was decubed with relative ease in ten or twenty minutes. More importantly, there were no flaws introduced from cubes sticking to the part or layers delaminating. Some of the success is directly attributable to the strength of the layer-to-layer bond as a result of the solvent lamination process. Upon closer examination of the surface with a microscope, it is evident that the pattern of fine crosshatches remains on the stair steps (see Figure 5). Thus, removal of this pattern and surface finish become issues to consider. Depending on the intended use of the part, it may not be necessary to improve the surface finish. However, if finishing is necessary, it is expected that normal grinding and polishing can be used to smooth the surface with no more difficulty than for parts made with other rapid prototype techniques. Therefore, the existence of the fine crosshatch pattern is not expected to pose any serious disadvantages.

A preliminary analysis of adaptive surface burnishing using simple geometries has revealed that surface burnishing is at least as effective as adaptive crosshatching. The advantages of surface burnishing compared to adaptive crosshatching are 1) burnishing the overlap zone generates less dust compared to cutting; and 2) the part surface is not left with a fine crosshatch pattern.

Mechanical Properties

An intensive characterization of the mechanical behavior of LOM SiC parts was made. MOR bars (4mm x 3 mm x 50 mm) were fabricated using the latest version ceramic LOM process and densified via reaction bonding. Over 50 bars were made in each of 6 different LOM runs. The results of the 4-point flexure tests are summarized in Table 1. It is important to note here that these specimens were tested as-received without any polishing.

Table 1 : four-point flexure test results for as-received (unpolished), reaction bonded, monolithic SiC specimens made with LOM.

LOM Run #	# specimens	Displace-ment rate (cm/min)	Flexure Strength (MPa)	σ (MPa)	Weibull Modulus
1, 2, & 3	10 each run	0.5	158	34	5.2
4, 5, & 6	10 each run	0.5	152	25	5.7
1	23	0.5	157	22	10.4
2	22	0.5	151	22	8.3
3	24	0.5	158	18	9.0
4	25	0.05	142	23	6.6
5	7	0.05	142	20	8.2
6	8	0.05	154	10	17.5
5	22	0.005	152	21	8.7
6	21	0.005	165	23	7.6

The 4-point bend strength of the unpolished SiC specimens is about 150 MPa. It is not valid to compare this strength to that of commercially available SiC because of the effect of polishing and chamfering in the case of the latter. In general, the strength of reaction bonded SiC is not expected to be as high as sintered SiC, which is approximately 400 MPa [7]. With proper preparation, the bend strength of LOM SiC is expected to significantly increase from 150 MPa, most likely by a factor of two. If this is found to be the case, then the bend strength of reaction bonded SiC will compare favorably with that of similar commercially available material made with conventional techniques.

The consistency of the bend strength from LOM run to run and within each LOM run is noteworthy. This consistency is characteristic of SiC as a material in general. The fact that the bend strength does not change with strain rate indicates that this material does not exhibit slow crack growth, another characteristic of SiC in general. Thus, in two more instances, LOM SiC compares favorably with commercially available material.

A photomicrograph of reaction bonded SiC (Figure 6) illustrates little evidence of a layering effect. In addition, low porosity indicates effective infiltration during reaction bonding.

Ceramic Matrix Composites (CMCs)

The fabrication of continuous fiber CMCs with LOM is another objective of this program. SiC/SiC is being used as a focus material system. From the onset, the two most critical issues were considered to be 1) the availability of preforms, suitable for LOM, which incorporate a high volume fraction of continuous SiC fibers; and 2) near-net-shape densification of the CMCs. Described in this section is the development of a suitable SiC/SiC preform for LOM and the various stages of the LOM process that dictated the preform's design. Issue 2 is being addressed through application of the reaction bonding process, as demonstrated with monolithic SiC, although detailed results are not yet available.

The approach to fabricating CMCs with LOM involves the layup of separate, alternating monolithic ceramic tape layers and fiber/resin prepreg layers. The development of a SiC fiber (Nicalon^{TM}, Dow Corning) and furfural resin (FurCarb^{R} UP-440, QO Chemicals) prepreg was described in a previous report [3]. The furfural is a thermoset resin that serves a dual role: as a binder during LOM fabrication and as carbon source for the reaction bonding process. Layers are bonded through heat and pressure applied by a flat heating plate or iron; no solvent is necessary. The fiber/tape layup is subsequently post-cured and pyrolyzed, followed by reaction bonding.

Early attempts to fabricate CMCs with separate layers of tape and fiber were limited by two practical problems, illustrated in Figure 7. First, the required laser power to cut through a fiber layer is much higher than for a monolithic tape layer. Although the laser power can be adjusted accordingly, it is not possible to handle the problems associated with random variations in the layer thickness or fiber content. Specifically, if the laser does not cut completely through a fiber layer, it will not be possible to simply "snap off" the adjacent waste cube during decubing due to the connected fibers. On the other hand, it the laser over compensates and delivers more power than is required to a fiber layer, the monolithic tape layer below will be severely damaged.

The second problem associated with the use of separate layers is that the adhesion of a fiber layer to the top of a tape layer is significantly weaker than to the bottom of a tape layer. This effect is caused by the ceramic tape which contains a resin-rich side on the bottom. The decubing is impractical because it is difficult to separate layers at the strong interface without delaminating the adjacent weak interface in the process. Thus, the problems can be generalized as an inherent difficulty of working with two separate layers that have significantly different bonding and cutting characteristics.

The situation is resolved by combining the separate tape and fiber preforms into one preform during the prepreg B-staging cycle, as illustrated in Figure 8. This new preform, the "tape-preg", is a simple fiber-on-tape laminate that solves both the laser cutting and laminating problems by eliminating the weak interface so that each layer contains both fibers and monolithic tape. The laser cutting is improved because the fiber component is the first to be cut. Therefore, if insufficient power is delivered to cut the entire tape-preg layer, the remaining material will be ceramic tape which is easily "snapped-off" during decubing. If too much laser power is delivered accidentally, the tape-preg layer immediately below will be minimally damaged, since its surface is comprised of fibers. The decubing is also improved because all the layer interfaces are of the same strength. The only practical complication is that the part layer thickness is necessarily doubled, unless thinner monolithic tapes and fiber prepregs are used. In this study, the tape-preg thickness was 0.5 mm (0.25 mm ceramic tape and 0.25 mm fiber prepreg).

To test the effectiveness of the SiC tape-preg, a small scale turbine engine seal (Figure 9) was fabricated with the "Table-Top LOM" (TTLOM) system at University of Dayton [4]. This experimental system was assembled to study laser cutting of high performance fibers and build CMC parts throughout the research program. The apparatus combines a copper vapor laser with a computer controlled XY gantry, manually adjustable z-platform, and manual layer lamination via hot iron. With this apparatus, one is able to obtain high quality laser cuts, illustrated in Figure 10, as defined by steep cut channels, no fiber end damage, and a minimal resin burn-back zone. The turbine engine part was built with seven layers of SiC tape-preg alternating in a $0/90^{\circ}$ arrangement. It was built and decubed without any problems. The decubing process was more similar to that for LOM paper parts rather than that for LOM monolithic ceramics. The reason for this is that the tape-preg layers maintain a distinct interface, i.e. the monolithic layers do not migrate into the fiber layers and vice-versa. For this reason, the use of adaptive crosshatching was not required.

After decubing, SiC/SiC parts must undergo a resin cure cycle to complete the cure of the furfural resin and to provide additional consolidation. The turbine engine seal was fit with a negative made from LOM paper, placed in a vacuum bag set-up, and cured in an oven using the following cycle: 25-200°C for 7 hrs; 200°C for 1 hr. After this cycle, the part was physically robust. The microstructure is given in Figure 11. Notice that the layers are well compacted with little or no porosity present.

The next step in the post-processing cycle was simultaneous resin pyrolysis and binder burnout. This step was evaluated by pyrolysis of free-standing, 6-layer, 1-inch SiC/SiC squares in flowing argon. Early studies revealed that the laminates were prone to delamination during the pyrolysis cycle. A variety of cycle conditions were tested under the initial suspicion that the problem was related to inability of the pyrolysis products to successfully diffuse out. However, two general observations were made: the delaminations always occurred within the tape-preg layers, not between the tape-preg layers; and the layers tended to curl perpendicular to the fiber direction. Thus, it is more likely that the problem is caused by the shrinkage of the furfural resin and the differential bond strength throughout the CMC. Although the bond within the tape preg layers is relatively strong during the LOM layup process, it becomes a relatively weak bond during the subsequent cure and pyrolysis cycle as the furfural resin cures evenly throughout the bulk.

The delamination problem worsens with increasing mass loss during the pyrolysis cycle. When the cycle is stopped at 250°C, there is 6% mass loss in the composite and it is possible to obtain an undamaged laminate using a slow heating cycle (2.5–5°C/hr). However, when the cycle is advanced to 300°C, there is 9.5% mass loss and the sample is delaminated. Based on thermogravimetric analysis, the laminates are expected to lose 20% mass through 700°C. It appears that to solve this problem a strategy involving only adjusting the heating rate will be unsuccessful. Alternative solutions are suggested. The first involves applying pressure to tape-preg laminates during pyrolysis. In an initial test, a sample that was placed under 15 psi pressure still delaminated during the pyrolysis cycle carried out to 300°C. Higher pressures will be investigated. A second strategy involves lamination of fiber layers only, omitting the tape layers. This strategy was successful in an initial study when a 10-layer laminate made of fiber layers survived the pyrolysis cycle through 550°C without delaminating. A third approach is to reconsider bonding separate layers of tapes and prepregs. The most appropriate strategy of these three is now under evaluation.

Conclusions

The monolithic LOM process was made more reliable and less labor intensive through recent hardware and software improvements. Monolithic SiC parts can now be fabricated with ease via LOM and post processed to dense ceramic through reaction bonding. These parts exhibit comparable mechanical behavior to commercially available SiC specimens fabricated with traditional processes. The LOM process for making flat layer, continuous fiber SiC/SiC composites has been demonstrated to the point of making fully cured green parts. Additional work is needed to develop a fully effective pyrolysis cycle. Once achieved, reaction bonding of SiC/SiC is expected to be feasible using monolithic SiC technology.

References

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Illustrations

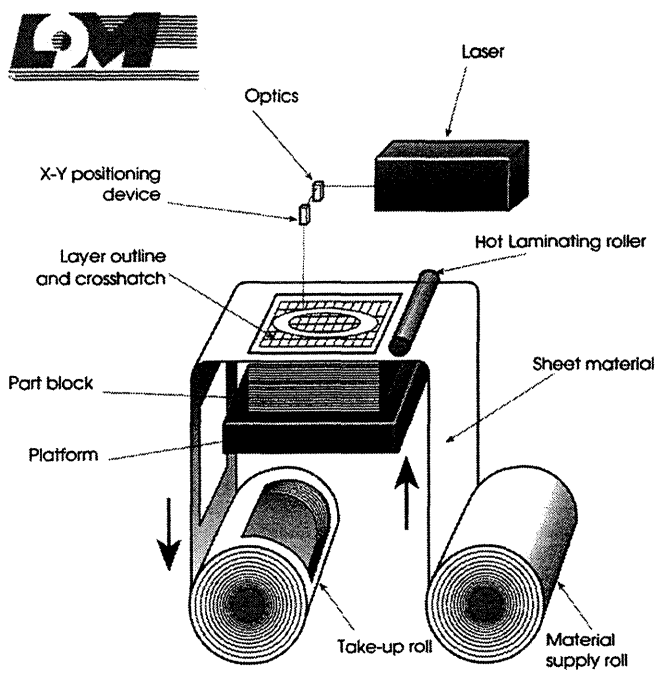

Figure 1 : Schematic of the LOM process (courtesy Helisys, Inc. [1]).

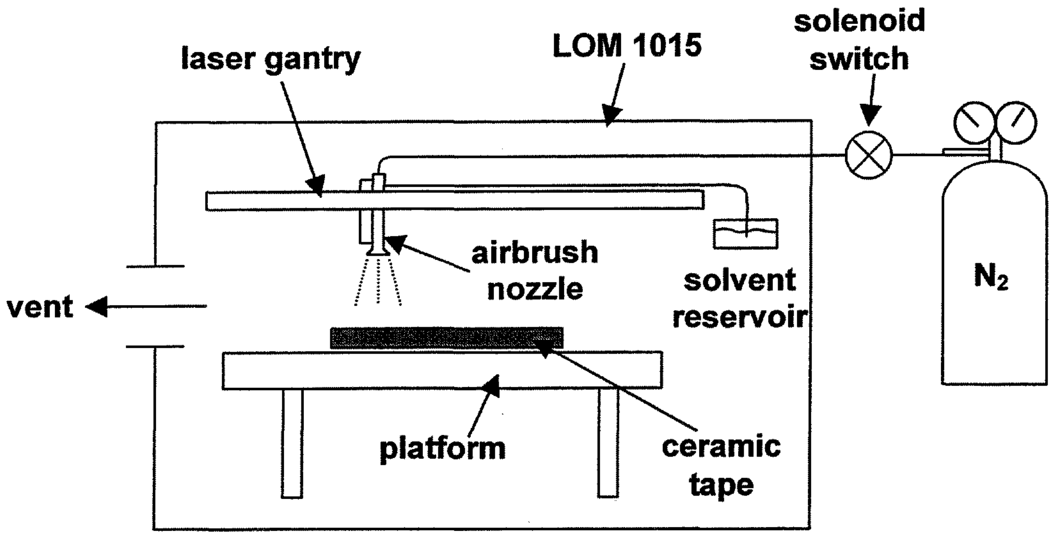

Figure 2 : Semi-automatic system for applying solvent to monolithic ceramic tapes.

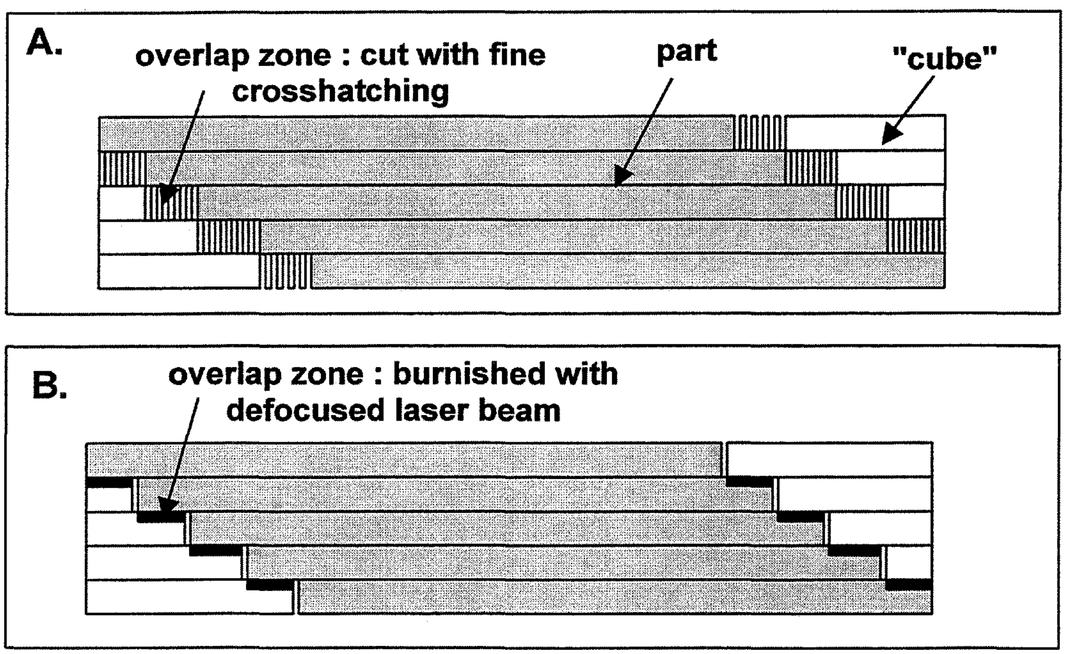

Figure 3 : Two strategies aimed at improving decubing by affecting the overlap zone between the waste cubes and the actual part : **a) adaptive crosshatching** and **b) adaptive surface burnishing**. This diagram is not drawn to scale; with the materials used in this study, the layer thickness was the same as the cut width (0.25 mm).

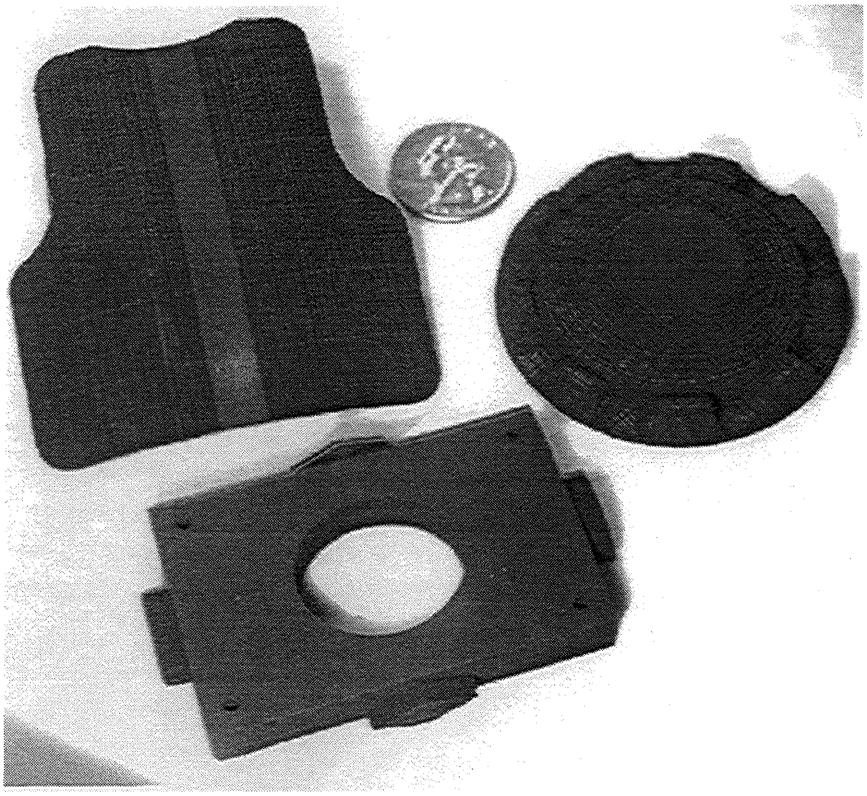

Figure 4 : Monolithic SiC parts made on a LOM2030 using the adaptive crosshatching software.

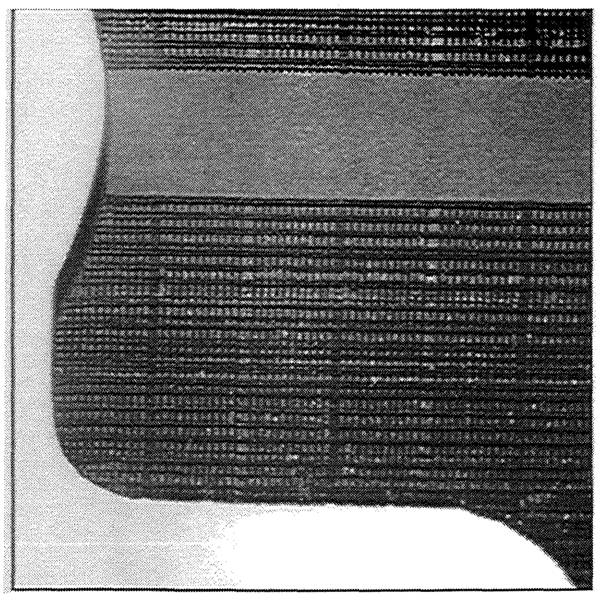

Figure 5 : Close-up of surface of body armor piece made with adaptive crosshatching.

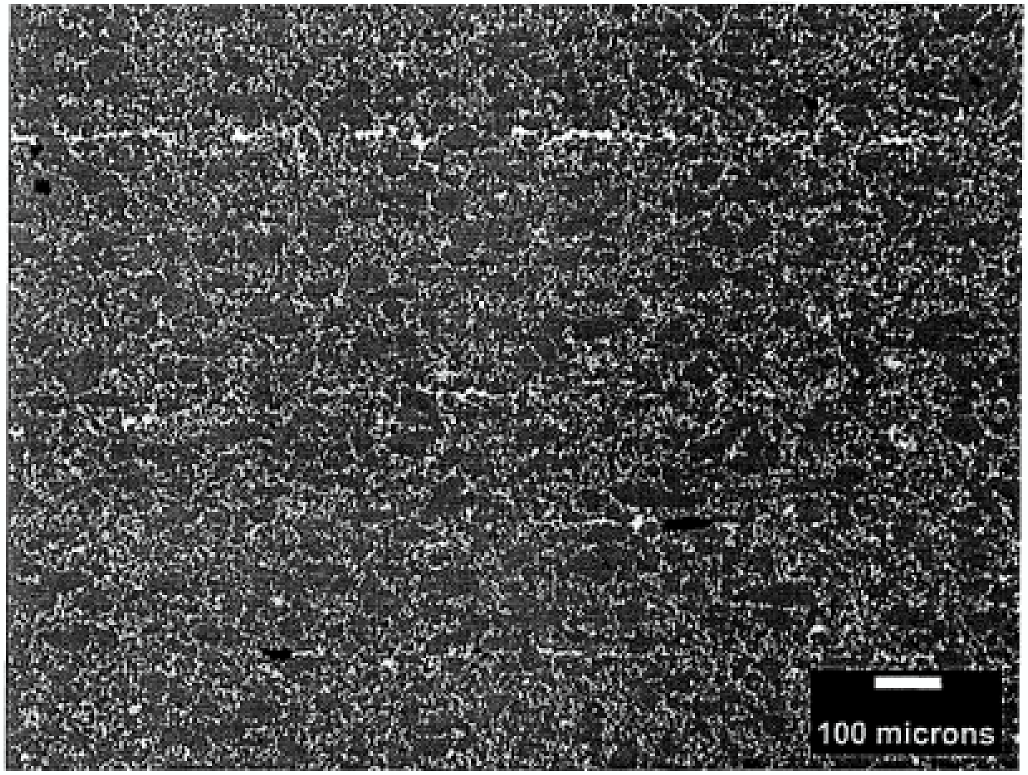

Figure 6 : Cross section of reaction bonded, monolithic SiC bar made with the ceramic LOM process.

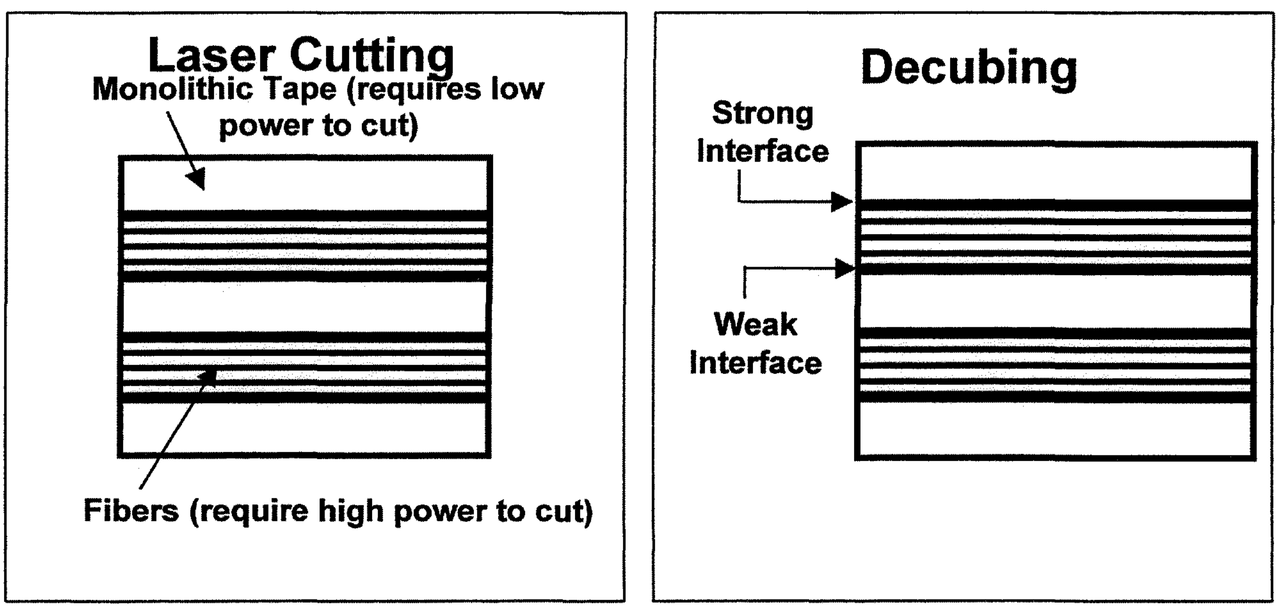

Figure 7: Illustration of origin of LOM processing difficulties for separate layers of fibers and monolithic ceramic tapes.

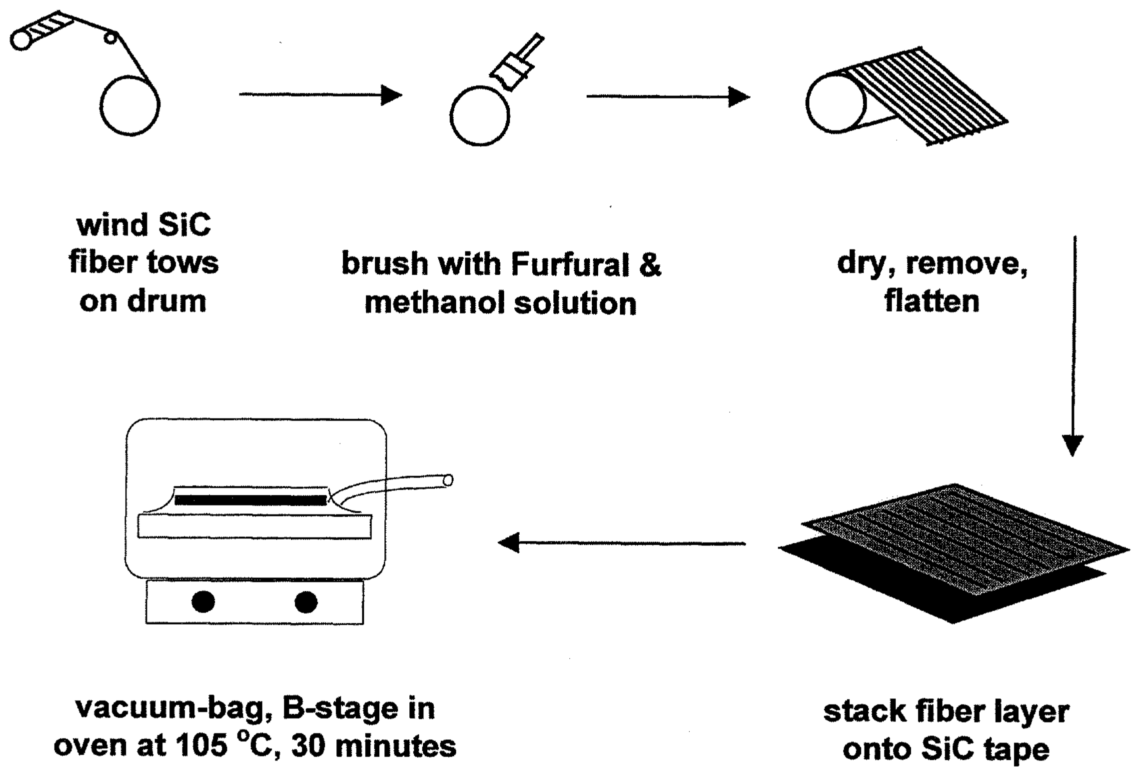

Figure 8 : SiC tape-preg fabrication process.

Figure 9 : 1/5 scale, turbine engine seal built from 7 layers of SiC tape-preg. As it appears, this part is fully cured but has not been pyrolyzed or reaction bonded yet.

Figure 10 : SiC fiber/furfural prepreg cut with a copper vapor laser. The fiber diameter is approximately 15 μm and the cut channel is approximately 80 μm in width. High quality laser cutting is characterized by the vertical walls, clean fiber ends, and minimal burn back zone.

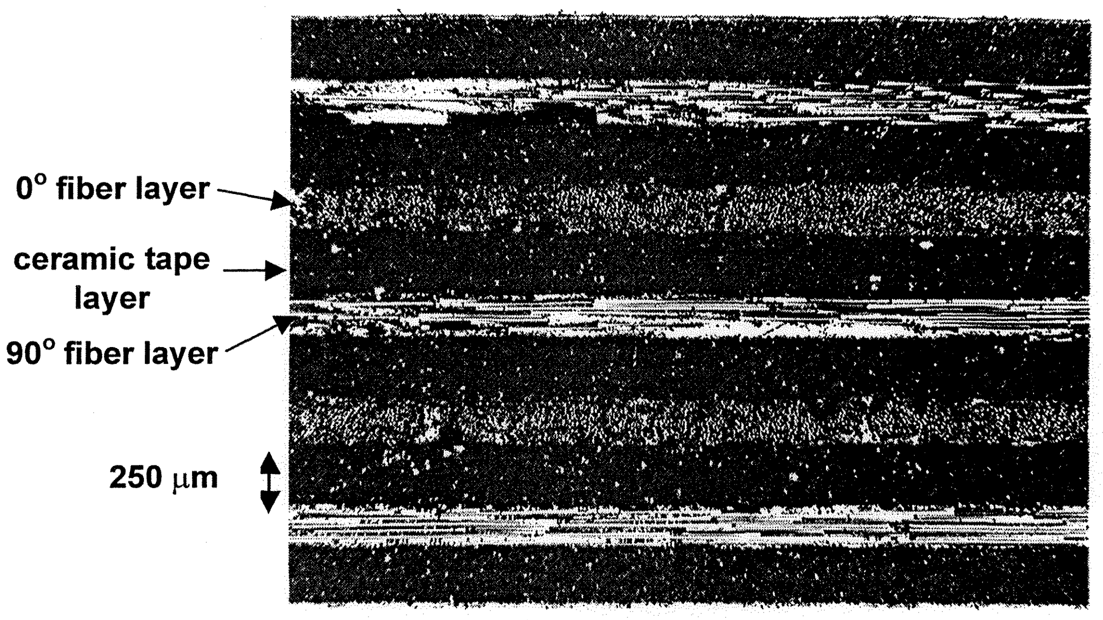

Figure 11 : Photomicrograph of green SiC/SiC composite made with "TTLOM" test bed. The sample has been fully cured, but not fully pryrolyzed.