Solid Freeform Fabrication of Continuous Fiber Reinforced Composites for Propulsion Applications

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INTRODUCTION

Monolithic ceramics lack the fracture toughness necessary to be considered for propulsion related applications. To be used for such applications, materials must possess low density, high elastic modulus, a low thermal-expansion coefficient, high thermal conductivity, excellent erosion and oxidation/corrosion resistance, and flaw-insensitivity. They will in many cases also be required to possess the ability to be joined, to survive thermal cycling and multi-axial stress states, and for reusable applications the materials must maintain the above attributes after prolonged exposure to extremely harsh chemical environments. The final and possibly most important attributes for these materials are the need to be of low cost and readily available in large quantities.

Fracture toughness of such materials could be improved by embedding continuous fibers into a ceramic matrix. This engineered material is called a ceramic matrix composite or CMC [1]. However, current state of the art methods for the fabrication of CMC materials such as chemical vapor infiltration (CVI) or polymer impregnation and pyrolysis (PIP) are expensive and time-consuming. Additionally, these processes cannot be easily adapted to rapid prototyping techniques, which would effectively reduce costs and fabrication times.

Recently, Advanced Ceramics Research, Inc. (ACR) has developed a low cost, flexible-manufacturing processes for ceramic based continuous fiber reinforced composites. This process, called Continuous Composite Co-extrusion (C^3), incorporates fiber tows into a ceramic matrix to fabricate ceramic-matrix/ceramic fiber composites. The C^3 process is the continuous extrusion of matrix material around a fiber tow. A flow chart illustrating the C^3 process is shown in figure 1. An interface material such as graphite is introduced between the fibers and the matrix to minimize the thermal expansion mismatch between the fibers and the matrix during the final consolidation step. The process is simple, robust and is widely applicable to a number of ceramic composite material systems such as Cf/SiC, Cf/ZrC, SiC/SiC etc.

The process begins by mixing the ceramic and graphite powders individually with thermoplastic binders and additives in a high shear mixer. The resulting ceramic powder/thermoplastic blend is pressed into a "green" rod. Next, the graphite powder/thermoplastic blend is pressed into a small diameter "green" rod. A hole of equal diameter to the graphite rod is drilled into the center of the rod and the graphite/thermoplastic rod is inserted. This green composite feedrod is then re-pressed and a hole is drilled in the center of the ZrC/graphite composite feedrod allowing the carbon fiber tow to pass through the center. Since the matrix and the interface are monolithic powders, the cost of the final composite could be lower than CVI and PIP based CMC's by at least an order of magnitude.

Recently, an innovative manufacturing technique called Advanced Tow Placement (ATP) has been developed Gillespie and co-workers [2] for thermoplastic and thermoset based polymer composite components at the University of Delaware Center for Composite Materials (UD-CCM). The ATP process is an enabling technology, developed originally for thermoset composites and more recently for in-situ non-autoclave consolidation of large-scale thermoplastic composite materials for High Speed Civil Transport (HSCT) applications. In this process, consolidation of the thermoplastic composite tows is achieved by the concurrent use of localized heat and pressure so that bonding is achieved at the newly formed interface and consolidation is achieved within the material. Figure 2 shows the schematic of the automated thermoplastic tow-placement process at UD-CCM.

Since thermoplastic binders are used in the fabrication of ACR's C[3] green CMC filaments, the ATP process originally developed for thermoplastic prepreg tows could be adapted to ceramic composites. The knowledge base of the ATP process for thermoplastic prepregs can be utilized to lay down ceramic tows reinforced with continuous fibers in the desired configuration. This allows the use of a proven technology for low cost, rapid fabrication of large complex ceramic parts. This process also allows the possibility to create complicated parts directly from a CAD drawing without human intervention. This process is called Ceramic Composite Advanced Tow Placement or CCATP process. In this paper, initial results with the CCATP process are presented.

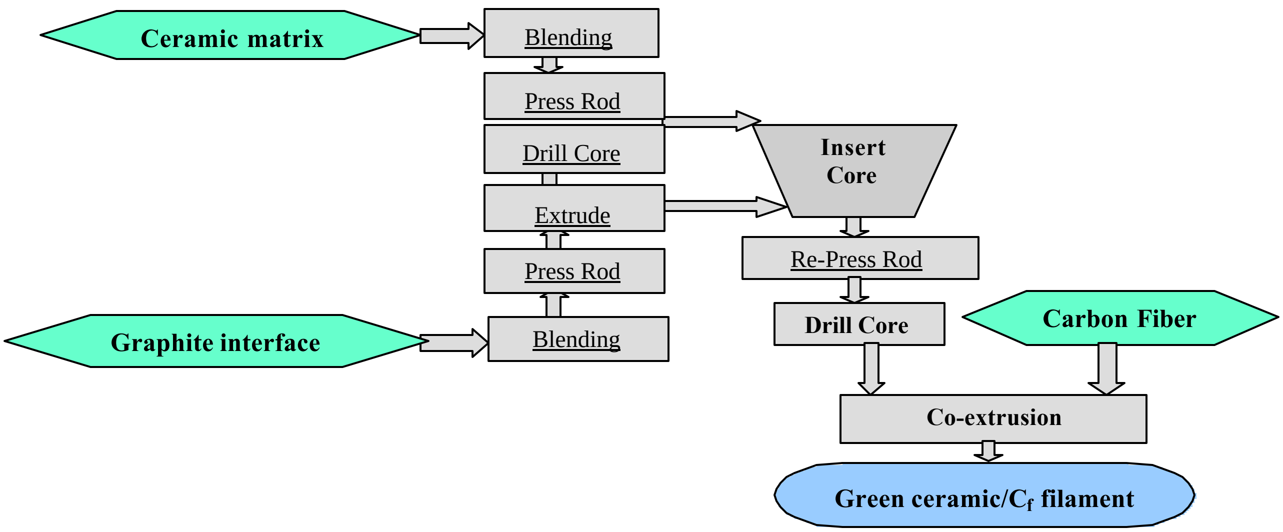

Figure 1. Flow Chart Illustrating the C^3 Process.

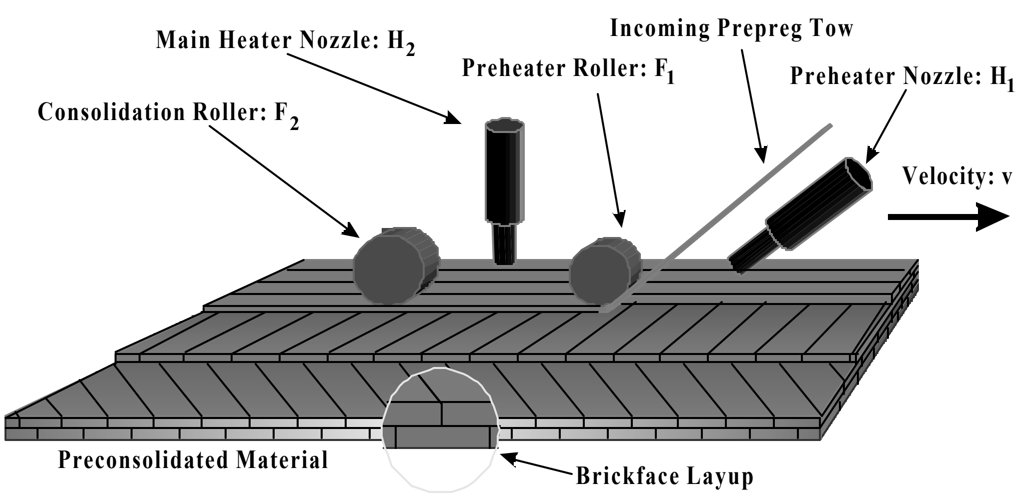

Figure 2. Schematic of the ATP process

EQUIPMENT AND EXPERIMENTAL PROCEDURES

EQUIPMENT

The automated tow placement system at the University of Delaware Center for Composite Materials was developed for rapid, low cost fabrication of fiber reinforced thermoplastic parts, and is shown in Figure 3. It employs the use of two hot-gas nitrogen torches to heat the material and two rollers to provide the pressures required for consolidation, as shown in Figure 2. The purpose of the first torch and roller is to preheat the composite surface and incoming tow together. The material is thus “tacked” to the surface with this roller. This tacking procedure is useful in that the fed material is carefully bonded to the surface and not pulled with the main consolidation roller. This tacking approach also aids in improving the efficiency of the cut and refeed mechanism. The second torch (main heater) provides supplemental through thickness heating to facilitate consolidation and bonding of the tow and substrate under the consolidation roller. These rollers provide the necessary forces to achieve complete intimate contact across the tow interface, and as a boundary pressure for preventing any internal void development.

Figure 3. ATP assembly at the UD/CCM Composites Manufacturing Science Laboratory.

The forces applied to both rollers are controlled independently using a series of pneumatic actuators. The composite tows can be placed in a regular repeating pattern or with brick-face symmetry. The brick-face geometry has the advantage that more homogeneity is achieved throughout the composite structure. All the processing inputs are controlled either manually or through a PID control scheme from a LabVIEW™ interface. An ABB IRB 6400 Robotic Work cell, shown in Figure 3, is used to control the motion of the placement head. This robot is capable of carrying a 120kg payload at automated speeds up to 7m/s and is accurate to 0.01mm. A computer-controlled nitrogen hot gas torch control system (not shown) is used to monitor and control gas flow rate and temperatures within both torches. The composite surface temperatures can be adjusted by either increasing the process velocity or by independent change of the nozzle heights. This novel temperature control method shows promise as an adaptive method for rapid control of surface temperatures and was recently patented by the UD-CCM [U.S. Patent No. 5,626,472]. The temperatures are measured and controlled with an AGEMA Thermal Imaging camera with a neural network based PID control system. The camera measures the viewable peak temperatures on the laminate surface and adjusts the nozzle heights accordingly to compensate for any deviation in set point temperatures. A Labview™ interface is used to input number of layers, ply orientation, surface temperatures, panel geometry, and process velocity. This interface can also be used in conjunction with a laser displacement unit to measure warpage during processing.

Test Materials

The ATP process for thermoplastics lays down prepreg tows, typically 0.125 – 0.2 mm in thickness, with the tow width depending on the hardware. The ATP head at UD-CCM can lay down 6.25-mm wide tows, while industrial machines, such as Cincinnati Milacron’s Gantry System can lay down tows as wide as 150 mm.

Fiber reinforced ceramic materials for this study were supplied by ACR and were in the form of green tows. The reinforcing fiber was carbon and the matrix was zirconium carbide based, in a low temperature thermoplastic binder. The tows were thicker than the thermoplastic tows for polymer matrix composites.

Initial tests with the ceramic tows revealed several important issues:

- The matrix was somewhat brittle and fractured easily under tension. This can pose a problem during tow placement as the tow is under tension to achieve good quality.
- Cut and re-feed mechanism on the head did not function consistently. This is due to the difference in thermoplastic (for which it was designed) and ceramic tows. Ceramic tows were manually cut to specific lengths and manually placed to simulate this.
- Adhesion between the tows and the matrix was not good. While this is not required at the green stage, fractures in the matrix result in exposure of bare fibers (in tension), causing inconsistent loading. This may not be an issue, as the actual fiber wet-out occurs during the sintering phase and can alleviate it. Further optimization of the interface thickness and type that is being carried out.
- The process temperature of the thermoplastic binder was low. Typical thermoplastic tows have process temperatures in the 300°C range. Therefore, lower torch temperatures were used.
- Over time, the matrix started adhering to the rollers. This occurred due to the rollers heating up past the melt temperature of the thermoplastic binder and resulted in the rollers peeling away the matrix from the tows. Solutions to overcome this problem are being devised.
- Minimal force was required for consolidation.

ATP Process Modification for Ceramic Tow Placement

Several process modifications were performed to obtain better quality material. These process modifications resulted in good material quality as shown in Figure 4 and 5. Note that, the tows were cut and placed manually to simulate the cut/refeed mechanism of the ATP head (Figure 6). Once the tows were placed, the robot performs the entire tow placement sequence to heat and consolidate tows.

Figure 4. Good material quality was obtained with modifications to the ATP head

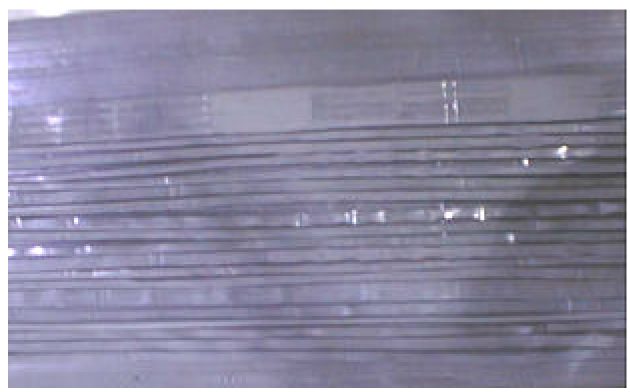

Figure 5. Photograph of ceramic tows placed manually. Upper half of the photograph shows tows consolidated by the modified ATP head

CMC Laminate Fabrication by Ceramic Tow Placement

Two green laminates were fabricated with the ceramic tows:

- 225 mm long x 75 mm wide [0/0] (9” long x 3” wide)
- 150 mm long x 75 mm wide [0/90/0] (6” long x 3” wide)

Figure 6 shows the ATP head in action during fabrication of both laminates. Typical microstructures are shown in figures 7 and 8 respectively. For both cases, the entire robot movement sequence is setup by computer programs developed for the ATP thermoplastic tow placement experiments. The torch parameters (temperatures, heights, and gas flow rates), consolidation force and head velocity can be controlled on the fly as inputs to the computer program. Final panel dimensions and lay-up sequences are also inputs to the program. Once these inputs are given to the program, it operates the robot in automatic mode and lays down the tows as specified. Green ceramic matrix laminates of any size (within limits of the robotic workcell), fiber orientation and material system can be fabricated by this technique. The current effort has not focused on optimizing process parameters, but on demonstrating the feasibility of rapid, low cost fabrication of fiber reinforced green ceramic composites.

Both laminates were successfully fabricated, though the tows were hand-placed due to the inconsistent operation of the cut and refeed mechanism. This did not allow for a through study of the overlaps and gaps during the automatic placement of tows. In addition, tension is necessary to maintain fiber straightness during consolidation and this was not possible at laminate edges due to hand placement of tows. Consequently, movement of tows during consolidation was seen. With automatic feed from a spool with tension, cut and refeed can overcome all these issues and identify correct level of overlap for consistent quality during consolidation.

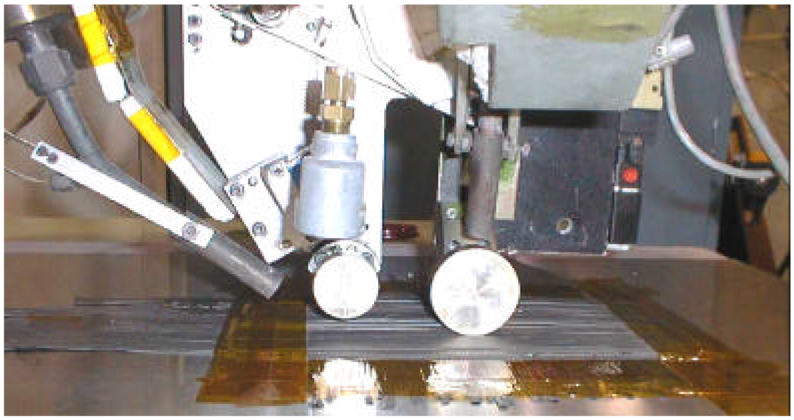

Figure 6. Modified ATP head consolidating 0 ceramic tows for the [0/0] laminate with top 0 layer showing

Figure 7. Typical cross-sections of rapid prototyped [0] Cf/ ZrC panels

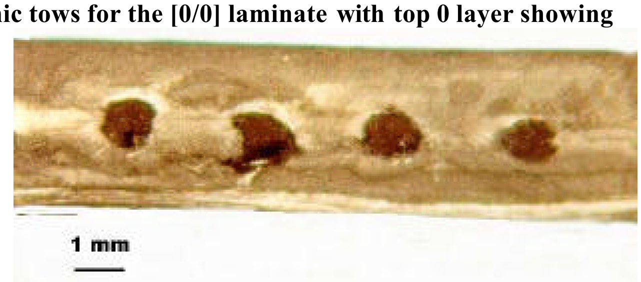

Figure 8. Typical cross-section of rapid prototyped [0/90/0] Cf/ZrC panel

Other components

Figure 9 shows a 6-inch diameter cylinder that was fabricated using the ATP equipment. This clearly shows the potential and capability of the process to fabricate complicated, full-scale components. This tube contains only three wraps of material.

Scale-Up Potential

Figure 10 shows the scale-up of thermoplastic ATP process developed in a DARPA RAPTECH (Rapid Technology) program led by UD-CCM with DuPont, Hercules/Alliant and Cincinnati Milacron. In this effort, UD-CCM demonstrated lab-scale viability and developed optimal process conditions for scale-up. Infrastructure for large-scale fabrication using gantry/robotic system exists.

Mechanical property and microstructural characterization of panels

Billets were hot pressed. The hot pressed panels were not entirely crack-free which indicated that the thermal stresses were not completely eliminated. An estimated fiber volume fraction of 35-40% was achieved after sintering. Specimens were tested in tension at a displacement rate of 0.2 mm/min using a load cell of 2500 lbs. at the University of Arizona. Representative samples were cut from the billets for testing. All the specimens exhibited good composite behavior, clear fiber pullout and in some cases, a stable loading pattern, with the load being taken up entirely by the fibers. It appears that the graphite interface thickness was too large for the composite to exhibit a high enough strength and good composite behavior at the same time. However, it is believed that these issues related to materials processing, though major, can be addressed and corrected. Typical tensile stress-displacement curve is shown in Figure 11 and 12, which shows good load transfer and the ability of the fibers to carry the load after the initial matrix has cracked. In many cases, the composite did not fail entirely and the fibers continued to carry the load. The test had to be discontinued at this point.

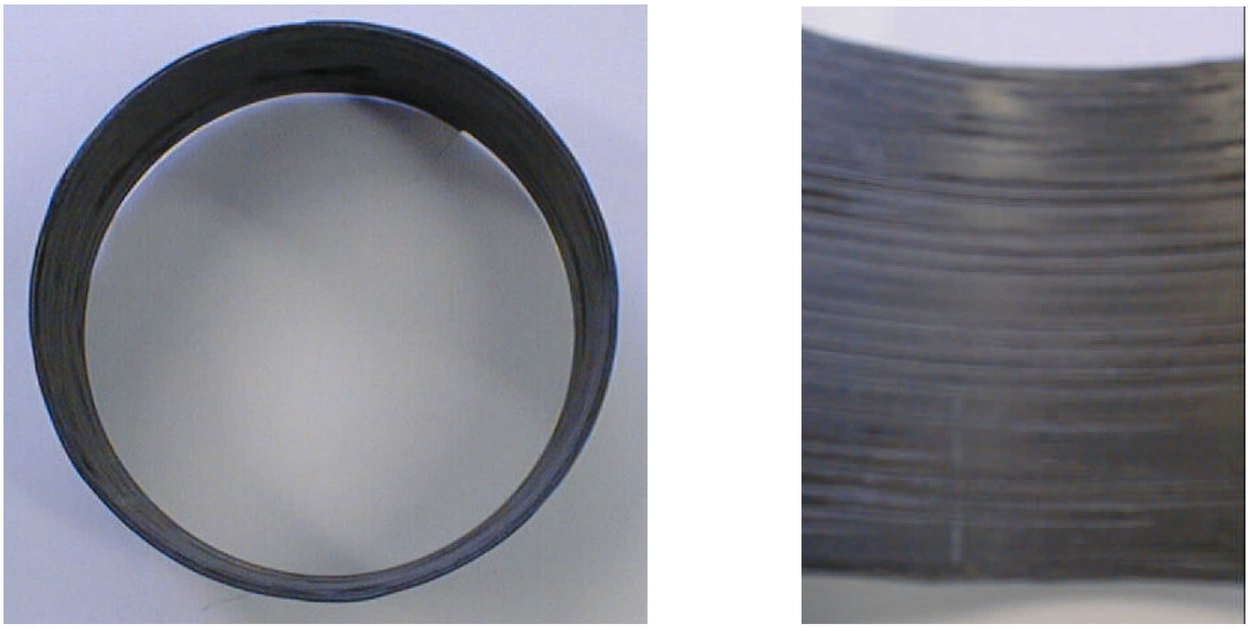

Figure 9. A six inch ZrC/Cf cylinder fabricated using the ATP equipment

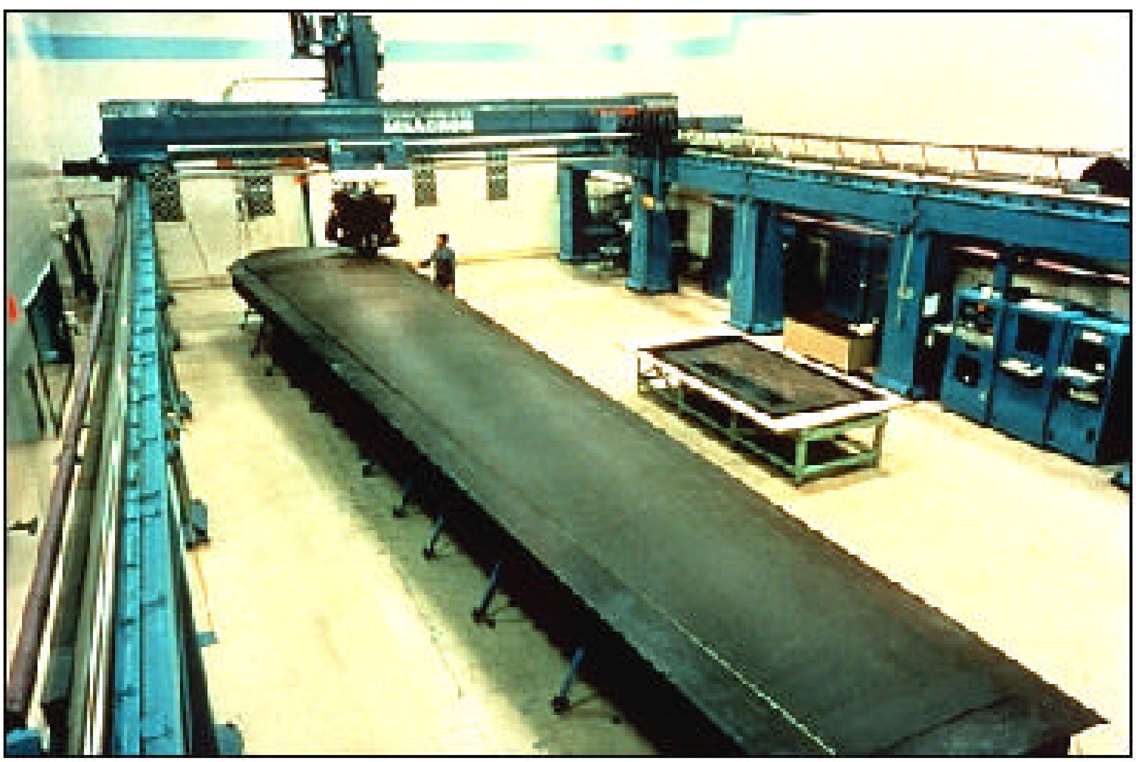

Figure 10. Automated Tape Placement head and gantry. (Picture courtesy of DuPont/Cincinnati-Milacron)

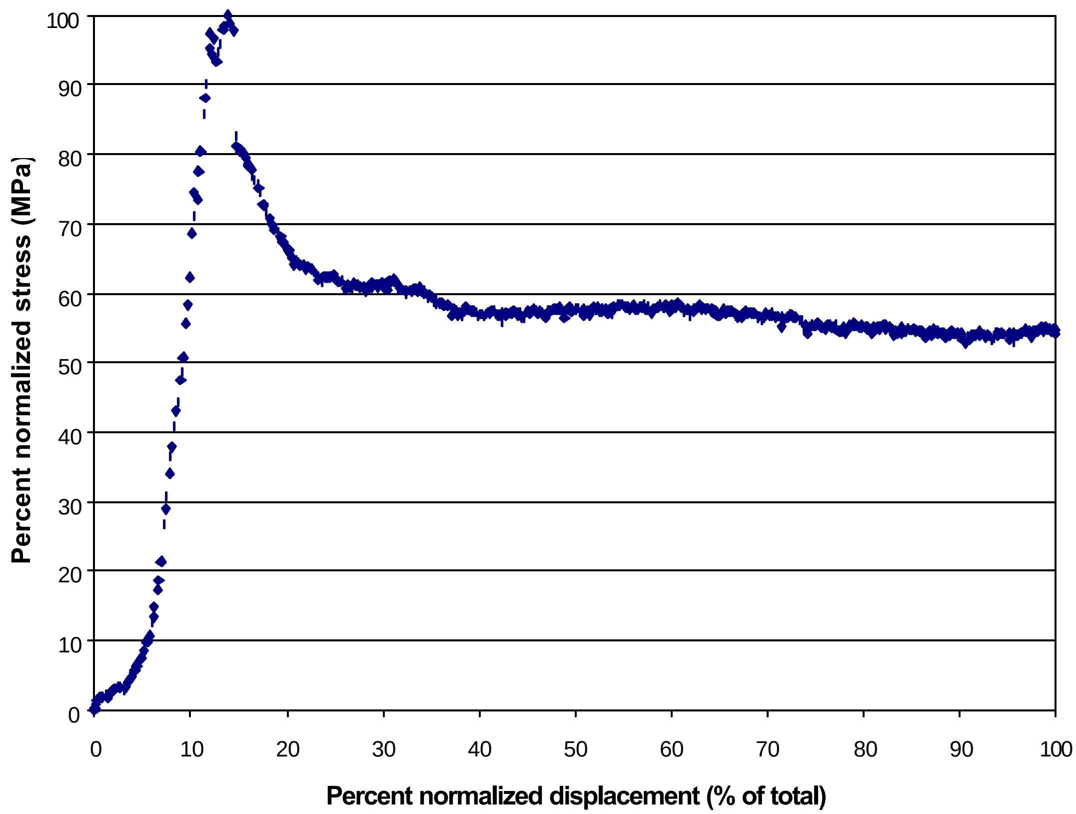

Figure 11. A typical tensile stress-strain curve for the rapid prototyped 0/90/0 panel.

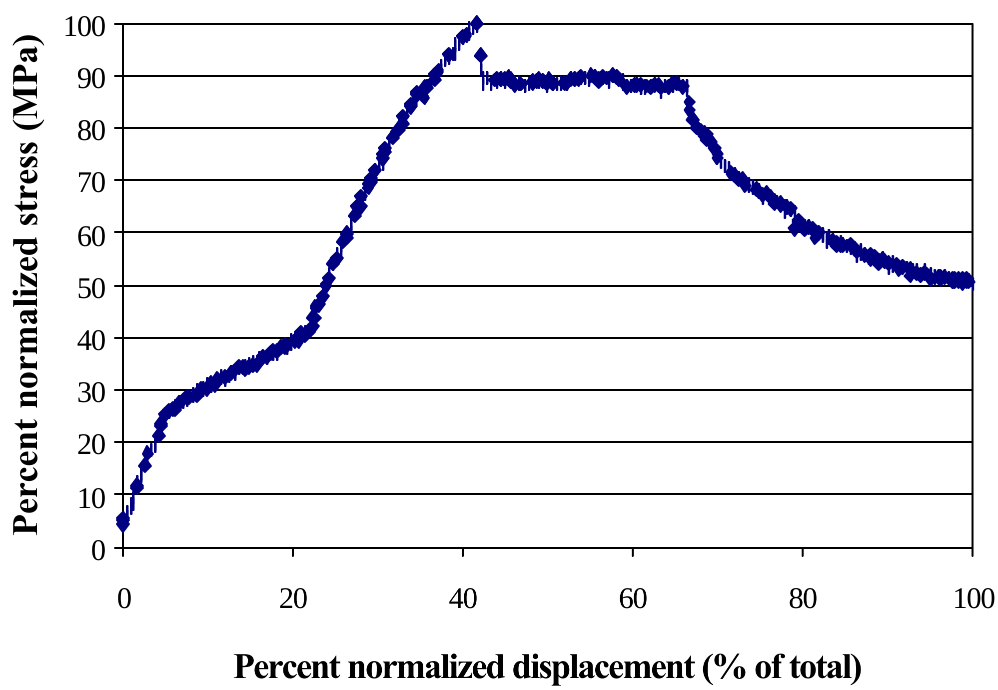

Figure 12. Typical stress-strain curve for a rapid prototyped Cf/ZrC composite specimen showing load transfer and the ability of the fibers to carry the load.

CONCLUSIONS

1. An innovative rapid prototyping technology to freeform fabricate continuous fiber reinforced ceramic matrix composites was successfully developed.
2. The feasibility of using the ATP process, with some modifications, for rapid fabrication of green ceramic composites has been demonstrated. [0/0] and [0/90/0] laminates were fabricated using the computer-controlled ATP head. Critical process parameters were torch parameters, consolidation force and process velocity. Several issues that need to be addressed are the automated cut and refeed system, parametric studies, optimization of process parameters and binder optimization.
3. 2D panels were rapidly prototyped using a fiber placement system similar to commercially available fiber placement equipment. A 6-inch diameter cylinder was also fabricated.
4. An estimated fiber volume fraction of 35-40% was obtained in the composites after sintering.
5. The composite exhibited good fiber pull-out and load-transfer from the matrix to the fibers, although further optimization of the interfacial properties are required to obtain satisfactory mechanical properties.

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