Fabrication of Multi-Layered Carbon Structures Using LCVD

Ryan W. Johnson, Scott N. Bondi, Daniel L. Jean,
Chad E. Duty, MingXuan Jiang, and W. Jack Lackey

Rapid Prototyping and Manufacturing Institute
Woodruff School of Mechanical Engineering
Georgia Institute of Technology
Atlanta, GA 30332

Abstract

Others have used Laser Chemical Vapor Deposition (LCVD) to create 3-D fibrous structures and helical springs. Current research efforts focus on the creation of more advanced three-dimensional carbon objects through the use of multi-layered deposition. Multi-layered structures require an understanding of interlayer adhesion and the propagation of geometric anomalies through multiple layers. An important aspect in minimizing these shape anomalies is the implementation of closed loop temperature control. Several laminated carbon structures are presented with discussions and observations about the fabrication process and visual characteristics of each. The major issues in using LCVD to create multi-layer carbon structures are addressed.

Introduction

Numerous previous attempts at constructing layered deposits using LCVD have been made. Such efforts have typically produced non-uniform periodic deposits or dimensionally unstable structures.[1] There is a belief that the general nature of the LCVD process is responsible for these irregularities. The existence of substrate protrusions and the creation of abnormalities in one layer of a deposit are thought to be amplified in each successive layer. This behavior stems from localized heating of surface irregularities causing increased local deposition rates. Online monitoring and control of the reaction is necessary to enable consistent and uniform deposition.

Recent efforts have been made to determine the feasibility of building multi-layered pyrolytic carbon structures using a temperature controlled LCVD process. All structures built for this objective were created using a multiple pass process whereby the substrate was either translated along one axis in alternating directions of travel or in a continuous circular pattern. The resulting structures were multi-layered carbon walls or cylinders conceptually similar to those presented by Messia, et al.[2] Theoretically, this construction technique will create layers that are intimately bonded producing a final structure that could exhibit either bulk solid or laminated solid properties. Many observations were made during the construction of the walls with regard to a new temperature control system and the general nature of the deposits. Some deposits were cut and polished so as to provide a view of the cross section of the walls and thus allow inspection of their integrity. Analysis of the cross sections and other features of the walls provide insight into the use of LCVD to create multi-layered structures.

Experimental Setup

Georgia Tech's LCVD reactor is powered by a 100 W CO_2 laser with a 200 µm diameter spot size. The system incorporates a fixed laser and reagent supply nozzle with several motion stages enabling the reactor to create three-dimensional objects by traversing and rotating the substrate.[3,4] The control of the plane geometry of the structures was accomplished by programming the substrate stages to move in the desired patterns. The most typical deposits that have been made in this manner at Georgia Tech have been of pyrolytic carbon; using the reagent gases methane and hydrogen at or below atmospheric pressure. All experiments described here used 75% CH_4, 25% H_2. The pressure in the reaction zone was held at 1 atm and the reagent nozzle flow was set to 300 sccm CH_4 and 100 sccm H_2.

Layered line growth using the LCVD process is dependant on several environmental variables that can greatly affect the rate and type of deposit that is produced. The most important of these is temperature. Some of the experiments presented below utilized a precision temperature control system. The temperature control was accomplished through use of a thermal imaging camera capable of resolving the temperature in the region of the laser spot to 3.5 µm per pixel. The camera's software allows for the creation of one or more 'Regions Of Interest' (ROIs) within which the average temperature can be calculated. The average ROI temperature is fed back to a PID controller for the laser power so as to maintain a target temperature as set by the operator. ROIs for these experiments were typically areas of about 0.246 mm^2 and temperature set points for the regions were varied between 1600 and 1700°C. Note that the ROI temperature does not necessarily correspond to the substrate temperature, but is a useful means for controlling the LCVD reaction.

Another factor in building layered structures is the speed at which the substrate is traversed beneath the laser spot, i.e. the scan speed. Many different speeds have been tested, and the tendency for heat to conduct away through the substrate during the initial stages of a wall enforces an upper limit on the initial scan speed. A lower limit is also imposed on the scan speed below which deposits may begin growing away from the substrate into fibers.[2,5] The fastest speed that has been used thus far with successful initiation under the given conditions has been about 42.3 µm/s and thus was used for these experiments.

A final factor in making deposits is the substrate material.[6] The Georgia Tech system uses a sacrificial substrate system, and these particular experiments used two graphite disk substrates with different levels of porosity.

Results

Experimentation with deposition of multi-layered carbon structures without a means of automatically controlling temperature and laser power yielded some interesting results that are consistent with the findings of others.[2] The procedure was typically to bring the reactor to running conditions and simultaneously begin translating the substrate and initialize the laser to a specific power level. Sometimes, the laser power was not altered throughout the course of the experiment while other experiments involved some systematic manual reduction in laser power as the wall height and number of layers increased.

The deposits exhibit non-uniform morphology and size. In particular, the laminated walls tend to develop large obtrusions on their ends while the center regions maintain a more uniform height as is shown in Figure 1.
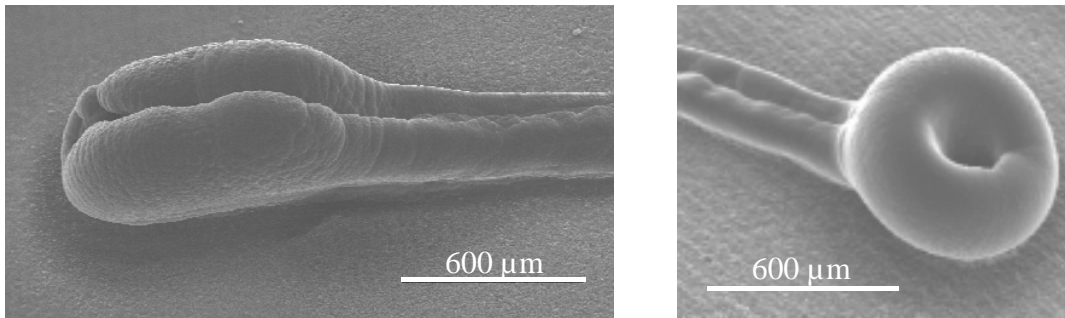

Figure 1. Carbon walls made without process control.[7]

The end obtrusions are likely related to several factors. One possible factor is the tendency for the linear translating stage to decelerate upon completion of a pass causing the end of the line to be exposed to higher temperatures.[7] A related factor involves the possibility of the stage pausing at the end of a pass causing the same phenomenon. In order to study the stage deceleration and pause factors, a control program was implemented to turn off the laser prior to the end of linear movement and restart the laser at the same position on the next pass. Figure 2 illustrates the concept of this control program. The implementation of the stage translation program had no significant impact on the end irregularity.
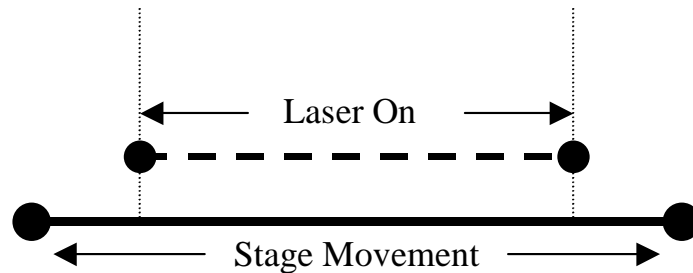

Figure 2. Diagram of stage control program used to study relationship between stage movement and line end irregularities.[7]

Another possible source of the obtrusions is related to heat transfer within the deposit and substrate. Initially, residual heat from the preceding laser pass leads to higher local substrate temperatures and an increased deposition rate. As the wall height increases, the nature of the heat conduction path changes such that the heat at the ends of the wall can conduct easily along the wall in only one direction, whereas the heat in the center region of the wall can conduct in two directions along the wall. During the deposition of such laminated structures as discussed above, observations were made through the thermal imaging camera as to the behavior of the temperature within the laser spot. It was observed that the ends of the lines exhibited higher temperatures earlier in the deposition process as is consistent with the shape of the resulting deposits. Active temperature control can eliminate these undesirable end effects.

Also noteworthy in Figure 1 is the appearance of a crevice in the center of the deposit. This 'volcano effect' could be detrimental to the use of LCVD in producing precise geometric objects, but has been shown to be a temperature or power density related phenomena.[8] According to Jean, the volcano effect for carbon using a methane precursor appears when maximum deposit zone temperatures exceed 2500°C.[7] This effect reiterates the need for a suitable temperature control system in the LCVD process.

Two grades of graphite substrates were tested for carbon deposition and the best results have been produced using the higher porosity graphite. It is theorized that low porosity graphite is more conductive and allows the heat generated by the laser spot to conduct away faster leading to longer deposit initiation times. Use of porous graphite would seem to encourage the creation of irregularities due to surface roughness; however, there were no apparent morphological differences between the deposits produced on the different substrates.

The implementation of automatic temperature control has allowed for significant advances in the ability to deposit uniform multi-layer carbon structures. The setup of the temperature control system used in these experiments was presented above. Figure 3 presents an image from the thermal imaging and control system during wall deposition.
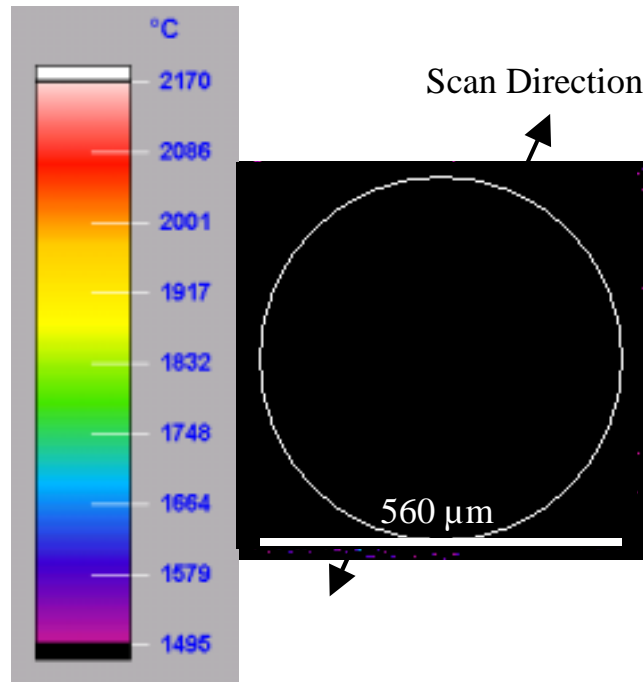

Figure 3. Thermal image captured during deposition with temperature control.[7]

Laminated deposits created using the temperature control system exhibited reduced occurrences of end obtrusions and the volcano effect. The elimination of the end effects with temperature control is due to the system's ability to automatically compensate for the increased local temperatures on the line ends by reducing laser power. Experimentation showed that the volcano effect could be eliminated by maintaining a temperature set point below 1700 °C for the given ROI. Figure 4 illustrates a typical laminated carbon wall built using the stated conditions.
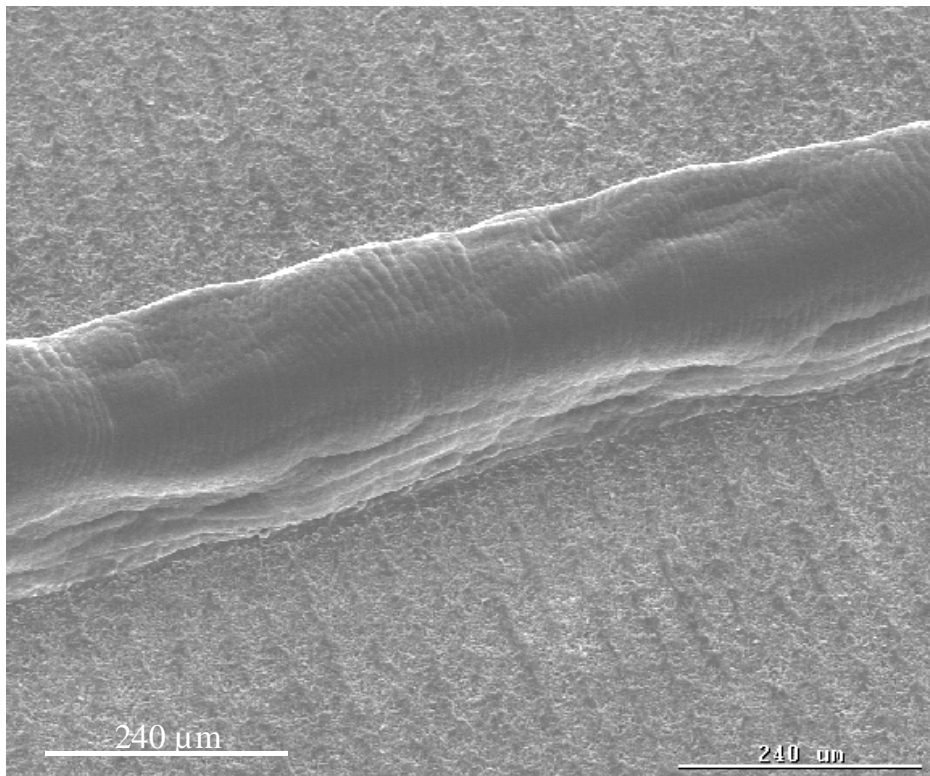
Figure 4. Twenty pass wall deposited using temperature control.[7]

The surface morphology of the walls was examined using a scanning electron microscope (SEM). Figure 5a illustrates a view of the top surface of a wall showing a rippled form. Figure 5b depicts the side of a wall. The side appears homogenous yet slightly stratified in accordance with the individual number of wall layers.
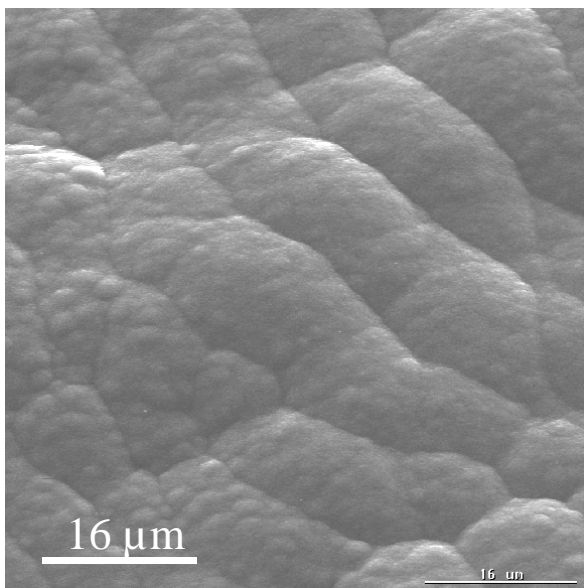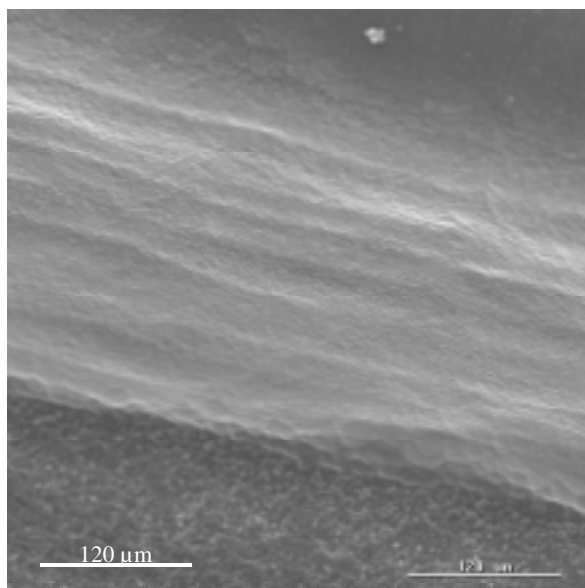
(a)   (b)

Figure 5. Surface appearance of carbon walls.

Examination of Microstructure

Internal analysis of the structures produced in these experiments yielded some interesting findings. Several samples were mounted in epoxy, cut, and polished to allow for examination of the cross section of the walls. Figure 6 is an example of such a cross section.
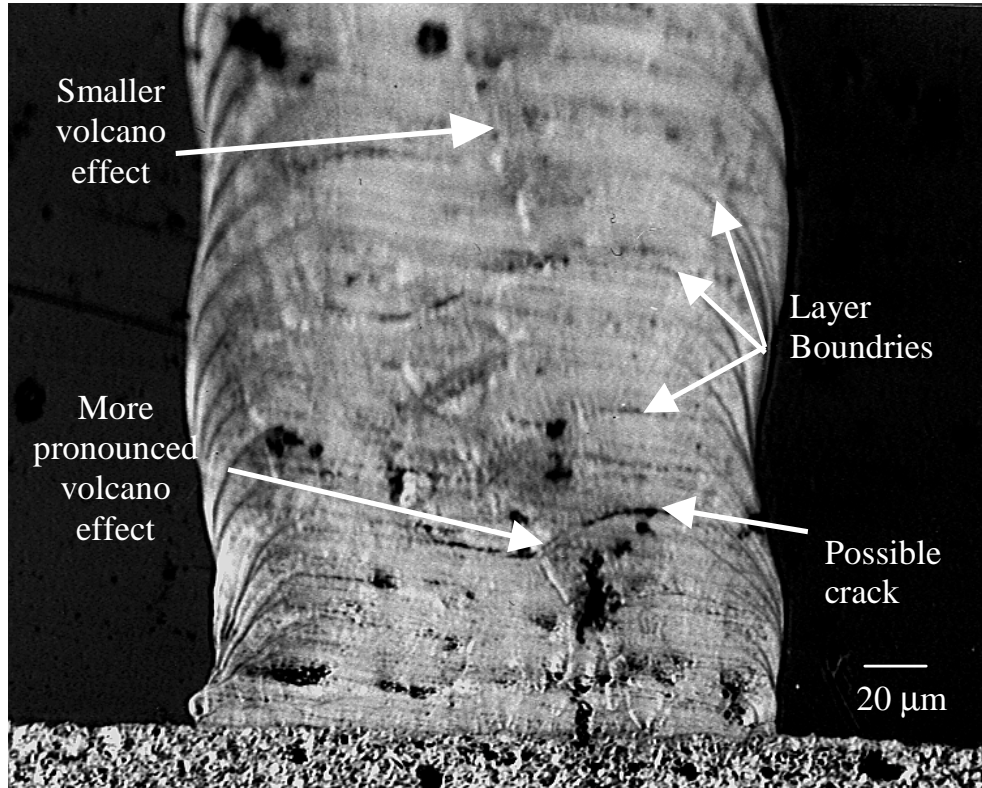

Figure 6. Cross-section of multi-layer carbon wall.[7]

One should first note the uniform density of the deposit. Individual layers of the wall can easily be seen in Figure 6. It is believed that some of the less defined black marks in the photo are artifacts of sample preparation such as residue from the polishing operation. The basic form of the deposit has the characteristic volcano shape, which appears to diminish with increasing numbers of layers. The diminishing of the volcano effect with height is evidence that a temperature controlled process can eliminate sizeable interlayer voids. An important feature observed in the cross section are cracks believed to be related to thermal stress between layers of deposit. One proposed method for addressing these cracks involves using a substrate heater to bring the substrate temperature closer to the reaction temperature and reduce the thermal gradients within the deposited structure. A substrate heater has been implemented into the reactor, but experiments to determine its effectiveness have not yet been conducted.

Some features of the deposit likely stem from a lack of robustness in the existing LCVD system. For example, the variation in the horizontal position of the layers as the height of the wall increases could be due to straightness error associated with the linear stage specified to be ±2.5 µm/25 mm. This can be seen in Figure 6, where the layers offset the width of the deposit

by up to 10 µm. The variations could also be caused by lack of rigidity in the mounting design for the stages.

Figure 7 is another wall cross section that illustrates the integrity of the multi-layer carbon walls. This sample does not show evidence of the volcano effect. The lower layers of the structure have a more rippled interface than the upper layers which again illustrates the importance of the temperature control process in dampening the effects of local abnormalities. This structure does not have the horizontal oscillations shown in Figure 6.
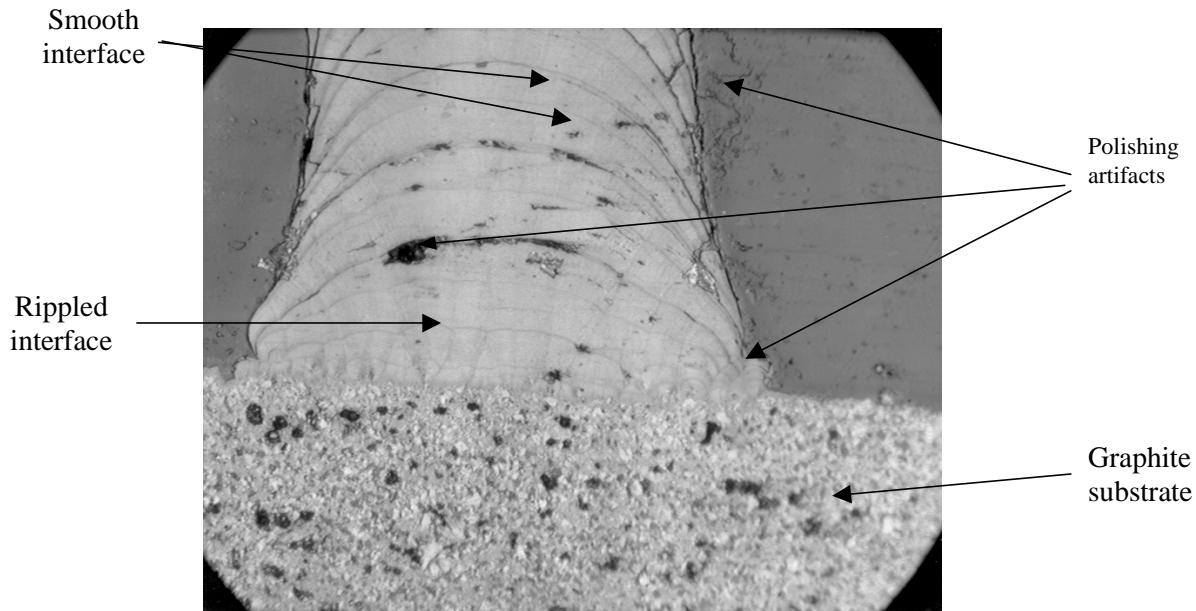

Figure 7. Cross section of wall without any volcano effects.

Conclusions

Experiments have shown that a temperature controlled LCVD process is capable of growing multi-layered pyrolytic carbon structures. The propagation of irregularities through the structures is reduced by the control process, resulting in a uniform deposit with a flat top and straight side walls. Viewing of the wall cross sections indicates a generally solid internal structure, free of large voids or defects. The interlayer bonding may be adversely affected by the thermal stresses associated with the laser heating. These thermal stresses could be the source of cracks shown in Figure 6. More testing is required to determine the extent of this apparent cracking and its impact on the functionality of LCVD multi-layered structures. In conclusion, we believe this work to be an important building block for the future creation of more complex 3D layered structures.

Acknowledgements

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