

Selective Area Laser Deposition From Acetylene And Methane To Increase Deposition Control

B.R. Birmingham, G. Zong, J.V. Tompkins, and H. L. Marcus

*Center for Materials Science and Engineering
The University of Texas at Austin
Austin TX 78712*

Abstract

Selective area laser deposition (SALD) has been used to deposit carbon from acetylene. Working at the relatively high pressures required to produce high deposition rates can result in explosive uncontrollable growth. Previous computational modeling indicates that the energy released from the exothermic decomposition of acetylene to carbon may be responsible for this behaviour[1]. Since methane decomposes endothermically to form carbon over certain temperatures, it is possible that methane addition to the process may help control the deposition rate. The purpose of this paper is to describe SALD experiments that were performed using various partial pressures of acetylene and methane as precursor in order to determine if combining an endothermic and an exothermic reaction effects the control of the SALD process.

Introduction

For the SALD of carbon to be a viable solid freeform fabrication (SFF) technique, the rate of deposition must be both high and controlled. Work done by Zong et al.[2] has demonstrated that deposition of carbon from acetylene at high pressure, 700 Torr, results in rapid uncontrolled growth. The carbon rod seen in Figure 1 is a result of this type of growth. The exothermic decomposition of acetylene into carbon and hydrogen, although it involves several intermediate reactions may be characterized as follows.



It is believed that the energy produced by this decomposition combined with the energy input from the laser is responsible for the runaway tendency of the deposition process. The deposition of carbon from methane is an endothermic process at low temperatures. That decomposition proceeds as follows.



It was postulated that the addition of methane to the acetylene, forming a dual gas precursor, would generate an environment where the endothermic methane decomposition moderates the exothermic acetylene decomposition. The result would be a deposition process with controllable high rates.

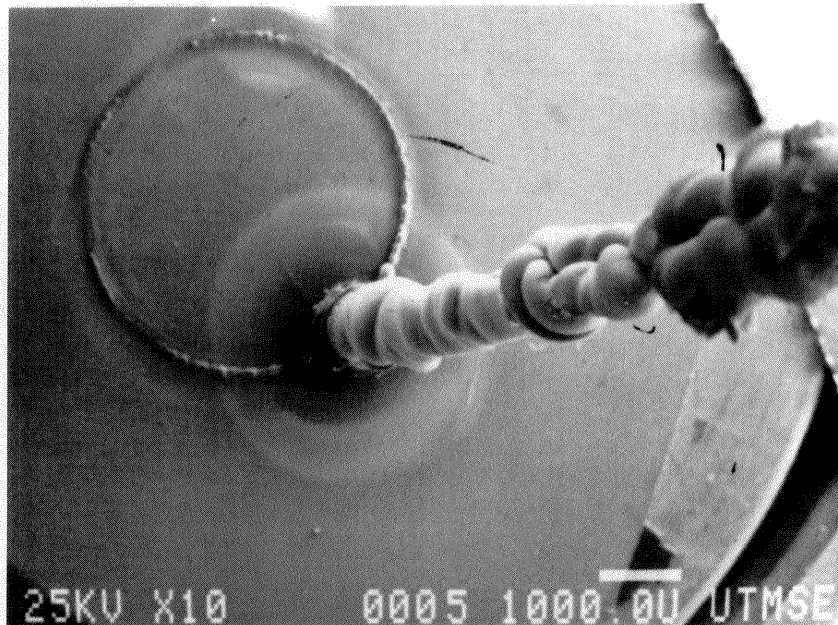


Figure 1: An example of explosive growth when depositing from 700 Torr acetylene[2].

Experimentation

The apparatus used to perform SALD consisted of a vacuum chamber capable of being filled with one or more gases, a CO₂ laser with focus waist of 100 μm , and a three axis motor driven table capable of moving the chamber and substrate relative to the laser in a programmable manner. The tests were performed in a static gas at the proper pressure. The volume of the chamber was large enough that accumulation of by-products or depletion of precursor was not a concern. The methane gas used had a purity of 99.97% and the acetylene purity was 99.6%.

The first tests to determine if this methane moderation effect would occur were performed at a constant 500 Torr partial pressure of acetylene. Two SALD runs were made. The first run used pure acetylene at 500 Torr for the precursor. The second run used a dual gas mixture of 500 Torr of acetylene and 200 Torr of methane for the precursor. Both runs incorporated a laser scanning pattern that would produce a 3 mm by 3 mm solid rectangle with thickness determined by deposition rate. Silicon powder, 10 μm particle size, was used for the substrate. Figures 2a & 3a show cross sections of the resulting structures, and Figures 2b & 3b are magnifications of the deposition surface. The cross section of the deposit made during the pure acetylene run, Fig. 2a, reveals a solid layer of fine structured carbon with a thickness of roughly 50 μm on the silicon substrate. Complete coverage has occurred. The cross section of the deposit made during the dual gas run, Fig. 3a, reveals a much thinner, incomplete layer of carbon on the silicon substrate.

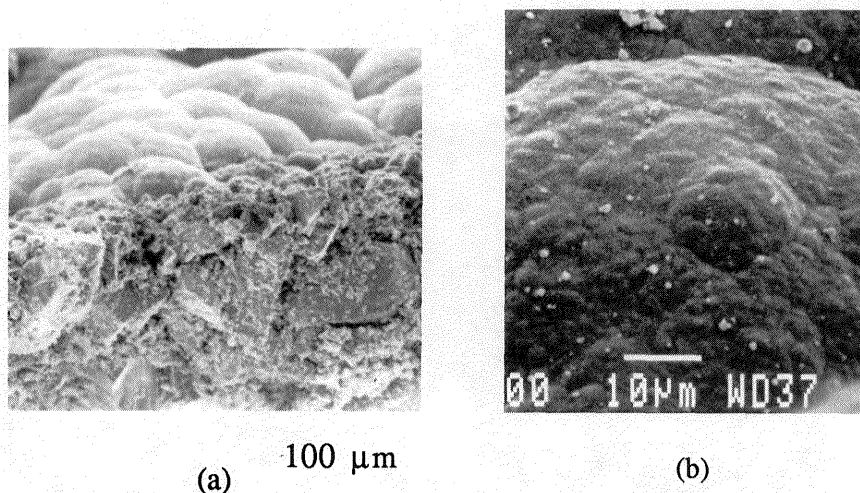


Figure 2: Deposition of carbon from 500 Torr C_2H_2 precursor a) Cross section of carbon deposit, 180X b) Deposition surface of carbon deposit, 1000X.

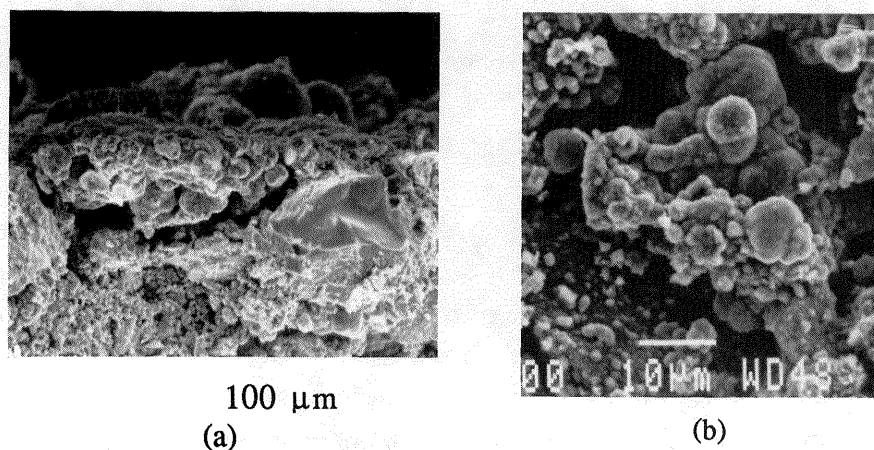


Figure 3: Deposition of carbon from 500 Torr C_2H_2 /200 Torr CH_4 precursor a) Cross section of carbon deposit, 300X b) Deposition surface of carbon deposit, 1000X.

A similar test was performed to verify these results. In this case the substrate was $16 \mu m$ SiC powder. All operating parameters were repeated except a line scanning pattern was used. This pattern would generate a 3 mm long line with thickness determined by deposition rate. Results from these tests reinforced the previous findings. Figure 4 shows two line deposits. The deposit on the left, made from acetylene, reveals a substrate completely covered by carbon. A very thin incomplete carbon layer produced from the dual gas mixture can be seen on the right side of Figure 4.



Figure 4: 3 mm line deposit on SiC. The line on the left was deposited from 500 Torr C_2H_2 precursor, and the line on the right was deposited from 500 Torr C_2H_2 /200 Torr CH_4 precursor.

To further explore this phenomenon, a third SALD test series was run. For this case, acetylene partial pressure was no longer held constant. Instead, total pressure was maintained at 500 Torr. A 3 mm line scan was again used for simplicity. Runs were made at 500 Torr methane, 250 Torr partial pressure methane/250 Torr partial pressure acetylene, and 500 Torr acetylene. Figures 4 & 5 show the results obtained.

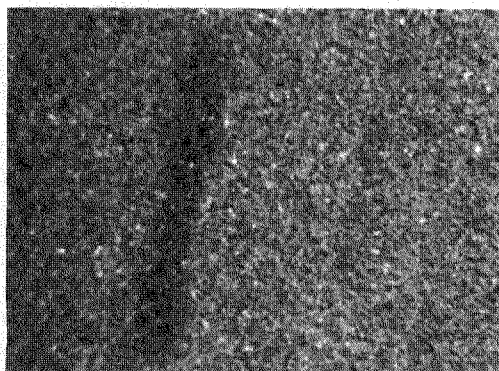


Figure 5: 3 mm line deposit on SiC. The deposit on the left was made from 250 Torr C_2H_2 /250 Torr CH_4 , and the line on the right was made from 500 Torr CH_4 precursor.

As discussed previously, the pure acetylene run, Figure 4, resulted in complete coverage of the substrate with fine structured carbon having a thickness of 50 μm . The 250 Torr partial pressure methane/250 Torr partial pressure acetylene run, Figure 5, resulted in a very thin incomplete layer of carbon on the substrate, and the pure methane run, Figure 5, resulted in virtually no deposition.

Discussion

By keeping the total pressure high, 700 Torr, and moderating the acetylene with 200 Torr of methane, rates at least as high as those seen during the 500 Torr pure acetylene test should have been achieved if other factors were not important. However, due to the substantial decrease in substrate coverage, it is apparent that rates were greatly diminished. One possible explanation would be that energy given off by the acetylene decomposition was absorbed by the methane without causing the methane to break down. This heat sink behaviour would lower the temperature in the area of deposition. According to Tesner[4], deposition from acetylene increases exponentially with temperature. Thus, a reduction in temperature would result in diminished acetylene breakdown and reduced overall rates. Another possible explanation deals with the different adsorptivities of methane and acetylene. If methane has a higher adsorptivity on silicon and SiC than does acetylene at the temperatures found in this process, then methane would displace much of the acetylene from the surface. Since methane decomposition rates are much slower than acetylene rates[4], the presence of higher methane concentrations at the surface would lead to lower deposition rates. A somewhat analogous situation has been reported by Bäuerle[5]. In that report, Ar, He and H₂ were added to acetylene. Rates were found to increase with argon addition and decrease for He and H₂ addition. The explanation was based upon molecular weight effects on thermal diffusion. The higher molecular weight material, Ar, would not diffuse to the deposition area as readily as acetylene resulting in increased effective acetylene pressure and ultimately higher deposition rates.

The results of the test which maintained total pressure constant and varied precursor composition between pure methane and pure acetylene were expected. It has been reported in the literature [4] that deposition rate from pure acetylene goes proportional to pressure. Because the rates expected from methane are so low, even neglecting all the possible effects discussed above, dilution of acetylene by methane at fixed total pressure could only slow down deposition rates.

Morphology is as important to the viability of SALD/SFF as is deposition rate. Not only must the part be made in a reasonable time period, but of course it must be structurally sound. Work has been done to try to characterize the effect of dual gas versus pure acetylene precursor on morphology. Several examples of very dense fine grained carbon structures have been produced, thus demonstrating the fact that these morphologies are obtainable. Figures 6 & 7 show two structures, one made from pure acetylene precursor, the other from an acetylene /methane precursor. The initial hope was that as well as solving the explosive growth problem, the dual gas mixture would

promote a finer, more dense morphology. To this date, results have been inconsistent, and no real correlations may be drawn. It is felt that this idea warrants further study.

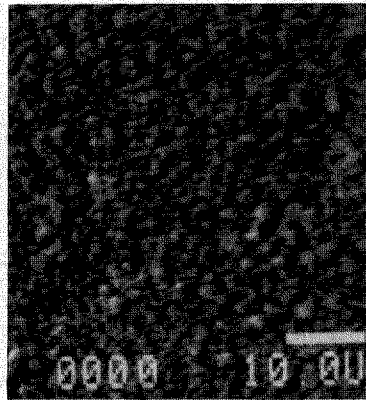


Figure 6: Carbon cylinder deposit, 500 Torr C_2H_2 precursor, 1000X



Figure 7: Carbon ring deposit, 500 Torr C_2H_2 / 200 Torr CH_4 precursor, 1000X

It is worth noting that even though the substrate is heated only by the scanning laser, there is evidence that temperatures at the laser deposition point may be relatively high. Figure 2a suggests some localized melting of the silicon substrate. Bergmann[3] provides an interesting look at the effect of temperature on heats of formation for methane and acetylene, see Figure 8. This would indicate that at least on a very local basis, both acetylene and methane decompositions are exothermic. What effect this has on deposition rate and morphology has not been addressed at this point.

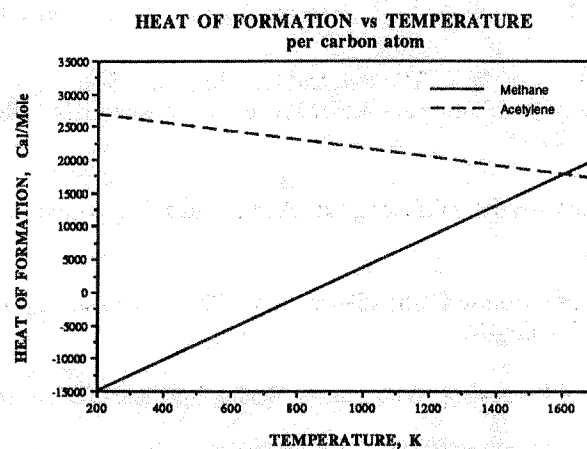


Figure 8: Heat of formation versus absolute temperature for acetylene and methane [3]. Note that the energies are per carbon atom. The acetylene value should effectively be doubled.

Summary

Tests were run in which selective area laser deposition was made from precursors of pure acetylene and precursors of the same partial pressure of acetylene plus an additional partial pressure of methane. Deposition rates, rather than increasing with increasing hydrocarbon pressure, decreased dramatically. Thus, it appears that methane has a retarding effect on the deposition of carbon from acetylene. No cause was demonstrated, but several hypothesis were presented. One explanation involved acetylene displacement at the surface by methane due to higher adsorptivity. Another possibility was that the additional gas served essentially as a non-reactive heat sink. The dual gas effect on morphology was briefly mentioned. No real conclusions were drawn other than to say that specimens have been made having good morphology, and further study is warranted.

Acknowledgements

This research is supported by the Texas Advanced Technology Program. Thanks are also extended to Ed Barth and Dr. Michael Schmerling for their help in obtaining the SEM photographs used in this paper.

References

- ¹ Jacquot, Yves, G.Zong, and H.L. Marcus, "Modeling of selective Area Laser Deposition for Solid Freeform Fabrication," Proceedings of The Solid Freeform Fabrication Symposium, edited by J.J. Beaman, H.L. Marcus, D.L. Bourell, and J.W. Barlow, Austin, Texas, August 6-8, 1990, 74-82.
- ² Zong, Guisheng, Yves Jacquot, W.R. Thissell, and H.L. Marcus, "Solid Freeform Fabrication Using Selective Area Laser Deposition," Plasma and Laser Processing of Materials," edited by Upadhya, Kamleshwar, TMS, 1991, 23-48.
- ³ Bergmann, Ernst D., The Chemistry Of Acetylene And Related Compounds, New York: Interscience Publishers, Inc., 1948, 2-3.
- ⁴ Tesner, P.A., "Kinetics of Pyrolytic Carbon Formation," Chemistry and Physics of Carbon, edited by Thrower, Peter A., 19, 1984, 65-161.
- ⁵ Bäuerle, Dieter, Chemical Processing With Lasers, Berlin, Springer-Verlag, 1986, 91-94.