# Gas-Phase Selective Area Laser Deposition(SALD) Joining of SiC Tubes with SiC Filler Material

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## Abstract

The laser-driven, gas-phase based SFF technique for joining together ceramic components with ceramic filler material, known as Selective Area Laser Deposition(SALD) Joining, was utilized in fabricating joined silicon carbide structures. Specifically, silicon carbide tubes were 'welded' together by depositing silicon carbide from a gas phase reaction. Two different precursor environments were examined, one a tetramethylsilane/hydrogen mixture and the other composed of methyltrichlorosilane. The quality of the joints were examined by bend tests and hermeticity measurements. In addition, the composition and morphology of the silicon carbide deposit was studied and is discussed here.

## Introduction

The technology for fabrication of robust ceramic parts lacks a proven and reliable method for assembling together complex designs from simple shapes. The challenges presented in joining together ceramic shapes arise from the very properties that make ceramics attractive. Their high melting temperatures preclude traditional welding techniques that utilize base material melting. In fact, silicon carbide and silicon nitride sublimate from the solid phase to their constituent gases and therefore display no melting characteristics. The poor wettability of ceramic surfaces with most metals presents many difficulties in brazing efforts. In attacking these challenges, a variety of novel ceramic joining procedures have been devised and examined. Diffusion bonding forms ceramic joints by diffusion of atoms across the joint seam at very high processing temperatures. Analogous to solid-state sintering, diffusion bonding suffers from the characteristic low diffusivity of ceramic chemical species and low ductility. Efforts to avoid these shortcomings have utilized metal foils, such as nickel, nickel-chromium and aluminum boride, as interlayers at the joint seam to enhance the diffusion and ductility[1,2,3]. Reactive metal brazing operates by using a metal filler in a traditional braze mixture to react with the ceramic surface and produce a more stable, wettable surface material[4]. The most promising brazes are silver-copper alloys with titanium or zirconium mixed in as the reactive agents[5,6].

This research program applied the gas-phase, laser-driven Solid Freeform Fabrication technique of Selective Area Laser Deposition(SALD) to the ceramic joining problem, in a process called SALD Joining. The initial, proof-of-concept investigation of this process at the University of Texas showed its feasibility by linking together alumina tubes, silicon carbide tubes, and silicon nitride tubes[7,8]. The UCONN research efforts studied in-depth the attachment of silicon carbide tubes together using silicon carbide filler material deposited in the SALD Joining process. The ultimate goal is to show the ability of gas-phase SFF techniques to fabricate separate ceramic parts and then *in-situ* 'weld' them together to form a complex ceramic structure. The tube geometry utilized in this program was chosen for convenience with the expectation that the SALD Joining procedure will work for other geometries and types of ceramic material, including those fabricated by SFF.

## Experimental Approach

SALD employs a high-powered laser beam to induce a thermal decomposition reaction of specific gases inside a vacuum chamber. The decomposition reaction leads to a desired solid product deposited inside the laser spot heated zone. The laser beam can be scanned by a motion control computer system to selectively deposit material in a desired pattern. SALD Joining utilizes the SALD technique to deposit solid product and use it as a filler material to join together ceramic parts. The UCONN joining chamber contains a rotational device to which the experimental tubes were attached. The joint seam could be scanned relative to the laser in several patterns, from a wiggle pattern back and forth across the seam to a simple stationary beam centered on the joint. A schematic of the tube rotation device is found in Figure 1. This scanning, as well as the tube rotation speed, was computer controlled by the Microsoft Visual Basic-based SFF Control System software. A stabilized, continuous wave(cw) 50 watt Nd:YAG laser from Excel/Quantronix served as the primary laser, operating at a 1.06 micron wavelength. The primary gas precursors used were a mixture of tetramethylsilane(TMS, $Si(CH_3)_4$) and hydrogen. Alternative gas precursors for silicon carbide deposition include methyltrichlorosilane(MTS, $SiCH_3Cl_3$) and a combination of silane($SiH_4$) and methane($CH_4$).

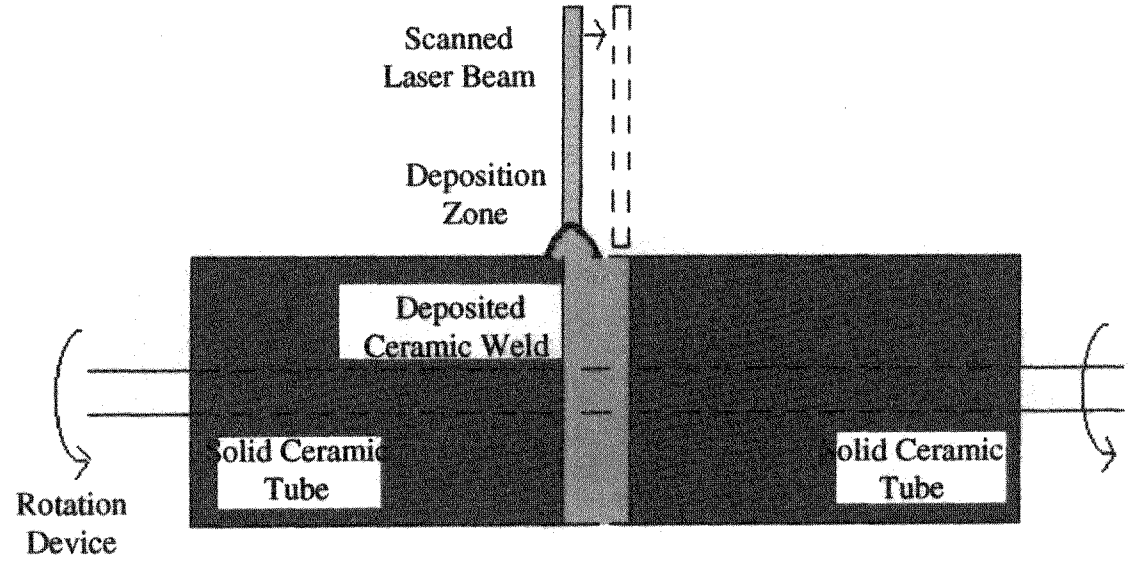


Figure 1: Schematic of Tube Rotation Joining Geometry

Two different types of silicon carbide tubes were used, a clay-bonded tube from Bolt Technical Ceramic of approximately 85 to 90% density and a DuPont Lanxide Composite tube of HiNicalon fiber in a silicon carbide matrix, referred to hereafter as fiber tube. The clay-bonded tubing came in ½ inch and 1 inch outer diameter sizes, while the fiber tube's outer diameter measured 3/8 of an inch. Experiments were run in two different manners, one with deposition temperature monitoring using an infrared pyrometer and one without the pyrometer. When utilizing the pyrometer, tube samples were weighed before and after deposition in order to calculate a mass deposition rate in correlation with the approximate temperature range. Otherwise, the samples were directly placed in the chamber. After a completed experiment, the sample underwent sonication for approximately 20 minutes to remove as much polymer reaction by-product as possible and then photographed using a Snappy frame-grabber video card and a color CCD camera. Further analysis was performed after the samples were catalogued.

## Experimental Results

Figures 2 and 3 display two successful tube joints. Both joints was fabricated using a 1 to 2 gas pressure ratio of TMS to hydrogen. Each tube section end was perpendicular to the tube wall, making a simple butt joint geometry. The ½" OD clay-bonded joint was deposited from a 1.5 millimeter wide wiggle scan program(i.e. relative to the joint seam), while the fiber joint originated from a stationary beam scan.

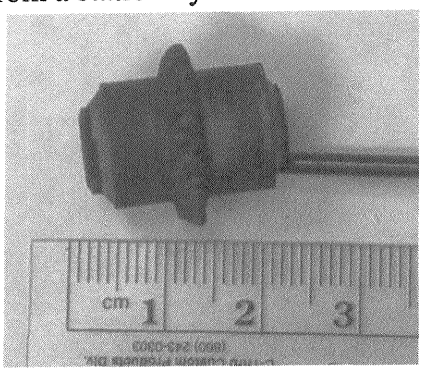


Figure 2: Clay-bonded SiC Tube Joint

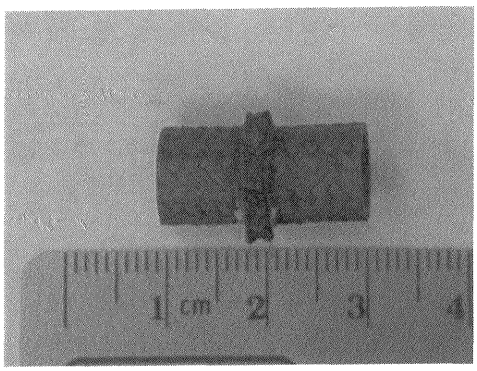


Figure 3: Fiber SiC Tube Joint

Cross-sectional micrographs of selected joints are found in figures 4,5,6 and 7, the first two from a clay-bonded tube joint sample and the last two from a fiber tube joint sample.

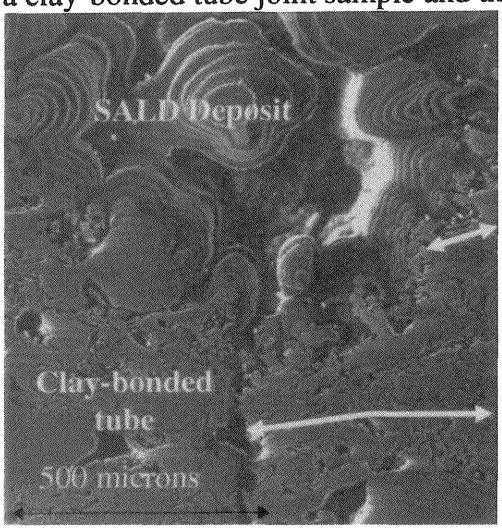


Figure 4: ESEM Image of Clay-bonded Tube Joint

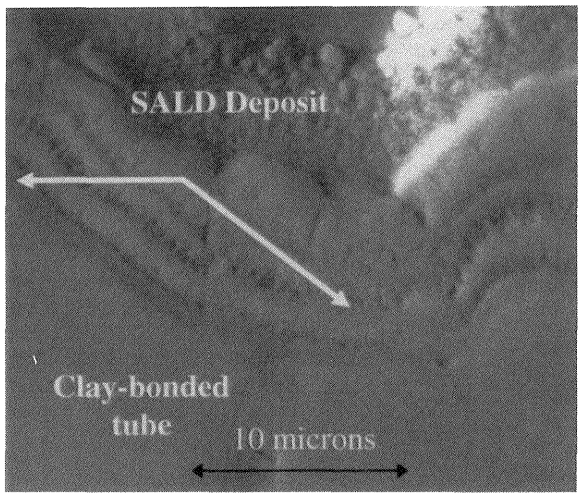


Figure 5: ESEM Image Close-up of Tube-Deposit Interface

Mechanical testing of the joints was accomplished using a cantilever-type bend test. One end of the joint remained stationary in a fixture while the other end was forcibly bent by the upward motion of a crosshead on an Instron tensile testing machine. The strength of the several joints tested showed low strength compared to that of the monolithic tube standards.

The hermetic quality of several joints was determined by connecting the samples to the deposition chamber and its mechanical vacuum pump by means of a Swagelok fitting and Tygon tubing. The joined structures were exposed to the running vacuum pump and the vacuum pressure in the chamber allowed to equilibrate, thus giving a measure of the lowest possible vacuum level possible for the joints. The results appear in Table 1, along with the vacuum level achieved with a monolithic tube standard.

Microhardness evaluation of the SALD material was performed with a Vickers indenter at a 500 gram load and 15 seconds indenter dwell time. The results are displayed in bar graph form in Figure 8. A total of 20 indentations were taken, and the average Vickers hardness number was 1446 kg/mm$^2$. The pure silicon carbide Vickers number has been reported as 3300[9].

Various samples of the silicon carbide SALD material underwent x-ray diffraction spectroscopy(XRDS). All showed the three peak configuration, at d-spacings of 2.52, 1.54 and 1.31 Angstroms, characteristic of beta silicon carbide, as has consistently been reported in silicon carbide CVD literature[10,11,12]. Higher temperature deposition material, in the 1300 to 1500 degrees Celsius range as measured by the pyrometer, displayed an additional peak at d = 3.35 Angstroms corresponding to the main carbon/graphite line

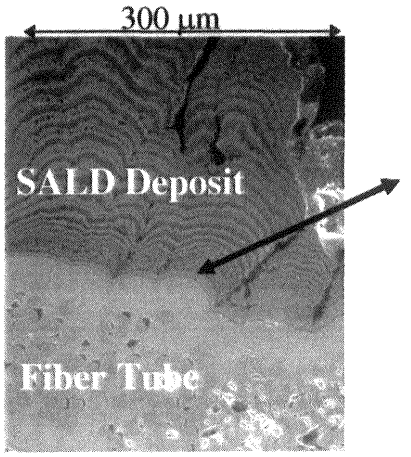


Figure 6: ESEM Image of Fiber Tube Joint

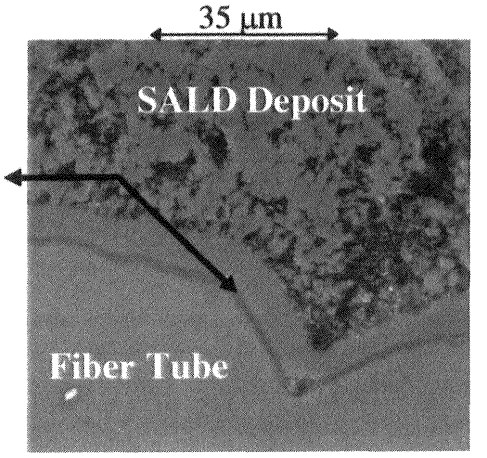


Figure 7: ESEM Image Close-up of Tube-Deposit Interface

| Sample | Steady-State Vacuum Level(in Torr) |
|---|---|
| ½" OD Clay-bonded tube standard | 9 |
| ½" OD Clay-bonded tube sample SJ#18 | 74 |
| ½" OD Clay-bonded tube sample SJ# 32 | 116 |

Table 1: Hermetic Quality of Tubes

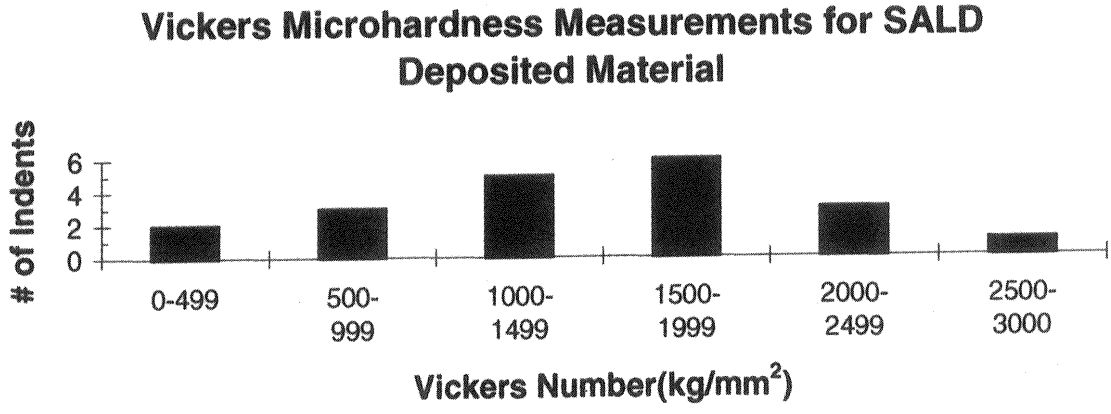


Figure 8: Vickers Hardness Determination of SALD Material

## Discussion

In this investigation, the SALD Joining process produced successful joints with two different types of silicon carbide tubing. The morphology of the deposit on each tube surface, in the Environmental SEM images above, shows excellent adherence with well integrated interfaces. The low mechanical response of the joined structures can likely be traced to the butt end joint configuration and not a function of the deposit bonding to the tube. This butt end alignment leaves a starting crack at the joint that is the length of the tube wall thickness. Future work will focus on minimizing this crack by beveling the tube ends with an expected improvement in the mechanical behavior. The hermetic seals of the tested joint structures were within an order of magnitude of the standard tube value. The better vacuum sealed joint, at 74 Torr equilibrium pressure, possessed a much smoother deposit morphology, while the other tested joint, at 116 Torr, deposited in a rougher columnar shape. We believe that a smoother deposit structure, i.e. more laminar than columnar, will produce better sealing by reducing the porosity and therefore the leak path. The microhardness values show regions of high purity silicon carbide as well as regions of very soft deposited material. The porosity inherent in the growth columns likely contributes to the response of these soft regions as does co-deposition of carbon in areas where the deposition temperature shot above approximately 1300 degrees Celsius. The hermetic sealing, microhardness uniformity and compositional uniformity will improve with the full implementation of the temperature control system. The deposition temperature can then be maintained in temperature regions where higher purity silicon carbide forms in a more even, layered manner.

The x-ray diffraction spectra obtained from the SALD silicon carbide material contained two interesting features. The first was broadening of the main peak at d = 2.52 Angstroms, leading to a grain size analysis. Over several samples, the average grain size was determined to be in the range from 5 to 40 nanometers. Further grain size analysis with dark field TEM was performed and yielded an average size of approximately 30 nanometers. The second interesting feature was examined only after Nuclear Magnetic Resonance(NMR) magic angle spinning characterization of the SALD material. The NMR data showed unexpected profiles compared to a beta silicon carbide powder sample. Closer analysis of the TEM imaging and of the fine structure of the x-ray patterns around the main peak, in conjunction with computer simulations of silicon carbide x-ray spectra[13,14], lead to the conclusion the SALD material is highly faulted. A publication concerning this examination of the SALD silicon carbide material is expected in the near future.

## Conclusions

The SALD Joining process offers great potential to solve the problems involved in ceramic joining. Monolithic joints, composed of the same material as the base material being 'welded' together, are possible. A dependable ceramic joining procedure could be integrated into a SFF fabrication system to build up large, complex parts from small, simple shapes in one step. This research shows that silicon carbide joints can be repeatedly fabricated with good mechanical, compositional and hermetic properties. Future work will focus on improving these properties and include tube end beveling, temperature closed-loop control and use of a second, higher power cw Nd:YAG laser. Higher purity silicon carbide tubes will also be joined together.

## Acknowledgments

The authors would like to recognize Drs. J.V. Tompkins and B.R. Birmingham for their initial SALD Joining work at UT-Austin, as well as Dr. K.J. Jakubenas for his work on the project as a postdoctoral fellow at the University of Connecticut. This research was funded in part by ONR Grant #N00014-95-1-0978.

## Footnotes

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