Selective Area Laser Deposition for Silicon Nitride Joining

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Abstract

Ceramic joining is a difficult step in ceramic manufacturing. Joining ceramics, in a chemically homogeneous way, can be performed through the repurposing of an additive manufacturing technique involving local deposition of ceramics from the gas phase. Selective area laser deposition uses a gas phase precursor environment and a laser heat source to form ceramic deposits. These deposits can be positioned with great spatial resolution; as such, it is possible to form the joint with the ceramic material to create a monolithic structure. Silicon nitride is explored as a joining material for silicon nitride work pieces. The experimental conditions are described and the joint formation is characterized.

Introduction

Ceramic manufacturing traditionally has suffered from the difficulty inherent in ceramic joining. To join existing ceramic work pieces after the green stage various methods have been employed. Few of these methods are capable of creating a monolithic joint, with a chemical composition that matches the work pieces. Brazing and glass joining are possible but both lower the part service temperature as well as contending with the poor wettability of many ceramics. Other joining techniques require high temperature and pressure, which could be both damaging to the work piece and not feasible for all applications.[1],[2]

The manufacturing technique of Selective Area Laser Deposition (SALD) is a localized chemical vapor deposition process. A focused laser heat source is used to thermally decompose a mixture of reactive gasses on a substrate within a pressure and composition controlled reaction chamber. The product of the chemical reaction is a solid ceramic and a residual waste gas. A computer control of an optic positioning stage in conjunction with the modulation of laser power allows for the deposition of arbitrary patterns. While the chemicals used as precursors are similar to those used in conventional CVD, a much greater control is possible over the geometry of the final deposition as apposed to the blanket nature of conventional CVD.[3] Additionally it is possible to create vertical growth utilizing multiple deposited layers without the need for any type of masking. The combination of X-Y positioning and the use of multiple layers can create three-dimensional structures. Previous work has explored the potential for manufacturing complex ceramic parts in an additive manufacturing mode.[4]

Selective Area Laser Deposition and Vapor Infiltration (SALDVI) is a modification of the above deposition process where decomposition occurs on the surface of, and around existing powder within a powder bed. The laser heats the powder and the reactive gasses diffuse into the powder bed. Thermal decomposition of the gasses occurs at the surface of the powder particles causing the growth of a ceramic matrix. Powder of a like composition can be used to make a monolithic material. Powder of a different composition can be used to create a composite effect. Subsequent layer by layer addition of powder allows complex geometries to be produced.[5]

This study explores the process of utilizing SALD and SALDVI approaches to form silicon nitride joints of silicon nitride substrates. The experimental parameters that can be manipulated, and the experimental setup used, are discussed. The resulting ceramic depositions and joints are characterized.

Chemistry Selection

The chemical composition of the deposited material is controlled by the chemistry of the precursor gasses. Some ceramic materials can be made through the pyrolytic decomposition of a single precursor while others require a more complex chemical reaction. Silicon carbide can be made through the decomposition of a single source, tetramethylsilane (TMS), ($Si(CH_3)_4$), with the addition of hydrogen, to reduce carbon contamination and non reactive dilution gases. The reaction that defines the formation of silicon carbide is:

$$Si(CH_3)_4 \Rightarrow SiC + 3(CH_4)$$

Hydrogen and helium are added in practice to minimize the formation of carbon.[6] To form silicon nitride, Si_3N_4, a combination of reactive gasses is required. The stoichiometric relationship for the formation of silicon nitride is as follows:

$$3(Si(CH_3)_4) + 4(NH_3) \Rightarrow Si_3N_4 + 12(CH_4)$$

To promote the production of Si_3N_4 over SiC and SiCN an excess of ammonia is required. The relationship $f = TMS/(TMS+NH_3)$ can be used to indicate the relative amounts of the reactants. The stoichiometric relationship yields an f of 0.43; however, it has been documented that for f less than 0.1 is required to drive the reaction to the production of relatively pure Si_3N_4. Experiments were conducted using f values from 0.05 to 0.5 confirming the trend toward Si_3N_4 dominant composition.[7]

In practice the deposition of silicon nitride and other SALD deposits are best performed below atmospheric pressure in a partial vacuum. Besides the physical constraints of the system, the reaction chamber is designed for operation at below atmospheric pressure. It is necessary to keep the partial pressure of all reactants below their equilibrium partial pressure. If this is exceeded, reactant condensation will occur. In order to keep the correct concentration of ammonia and maintain the pressure below atmosphere it is necessary to keep the TMS at a lower partial pressure, which limits the available yield of Si_3N_4. A balance must be maintained so that there is the greatest yield of the decomposition product while keeping the overall pressure below atmospheric pressure. The initial total pressure must be kept sufficiently low as the yield of product gasses is in excess of the initial gases by a ratio of 12:7. If the total pressure becomes high enough, of the order of atmospheric pressure, a contamination film tended to form on the chamber window interfering with the laser beam.

Experimental Set Up

The SALD/SALDVI deposition system is ~10 liter vacuum chamber with a centrally located laser window, Fig.1. A sample stage is located beneath the window with various sample fixturing positions. A gas manifold controls the input gasses that do not need to be vaporized, H2, He, Ar, NH3. Separate ports allow the introduction of vaporized, volatile precursors such as TMS. Two pressure sensors monitor chamber pressure. A thermocouple gage is used to determine the quality of the vacuum produced by the mechanical pump, and a stainless steel diaphragm pressure gage is used to monitor the relative concentrations of the reactive gasses during their introduction. To decrease contamination the system is designed for temperature controlled multi-zone bake out. Waste and unconverted reaction gasses are diverted through a water trap neutralizer when the system is put under positive pressure. Duel mechanical pumps are used; one to pump the reaction chamber and one is used to pump the manifold between gas introduction stages.

The laser used in this study is an IPG Photonics 100 watt CW fiber laser with a 1070nm wavelength. A X-Y positioning stage supports mirrors and a focusing lens that direct the beam through the viewport. The focusing lens has a focal length of 150 mm, and in the current configuration, produces a 100 μm spot size, established by test ablation of a tantalum film. A computer control system is used to control the laser output and beam positioning. A custom designed Labview code was written to control the deposition process. Laser modulation can be controlled by a waveform and power is calibrated to an external power meter. The X-Y stage is controlled so that individual layers are composed of a variable spacing raster pattern and each layer can have its own unique geometry. The deposition geometry and scan line spacing are also controlled by the code. Motion control is a Proportional Integral Derivative feedback system, which controls servomotors with optical encoders. A schematic of the deposition System is shown below.

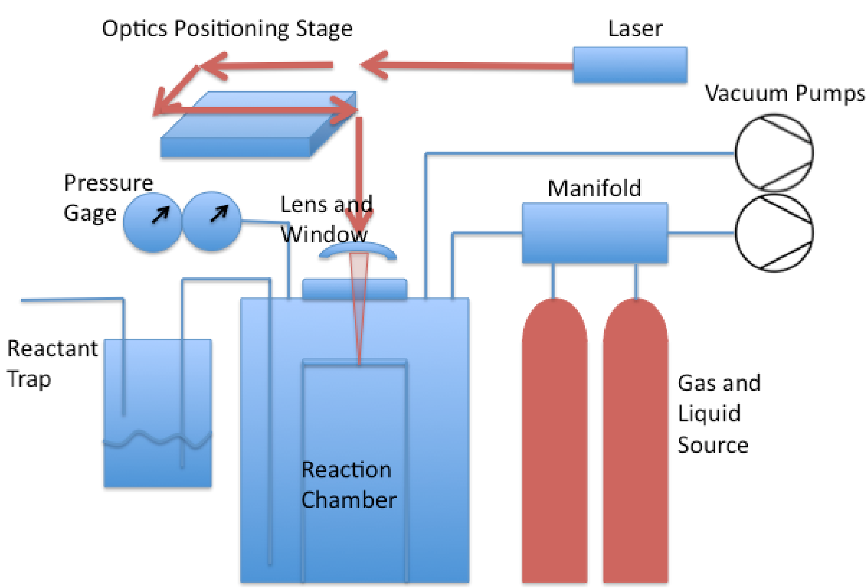


Figure 1: Experimental Deposition System Schematic

A flat titanium disk was used for surface deposits of Silicon Nitride. Scan rate, laser power, line spacing, geometrical design, and chemical composition were tested on this substrate. Another substrate consisted of a series of grooves machined into the disc surface with these grooves serving as a test bed for joint fill geometry. In order to evaluate the potential for powder infiltration deposits, the sample substrate used was a recessed dish filled with Si_3N_4 powder. Silicon Nitride joints were made by abutting two bevel-edged Si_3N_4 substrates both with powder fill and without.

Experimental Results

The SALD process has several parameters that must be evaluated to produce the best quality deposit. Laser power must be selected, so that decomposition can occur without uncontrolled run away growth. Scan speed must be considered in conjunction with laser power in order to get a consistent deposition rate. Initial tests were performed with a stationary beam to determine if growth is possible. Subsequent tests were performed at scan speeds ranging from 50 μm/s to 1500 μm/s. Scan speeds faster than 1250, were poorly controlled by the servomotor resulting in a non-uniform deposition and poor adherence to the programed geometry. 1000 μm/s is the speed where the most uniform deposits are formed.

The laser power was varied for this experimental series. The laser used was capable of producing 10-100 watts of power. For this type of experiment, considering the small focal size, this is too much power. The laser was passed through a 70% reflection beam splitter with the excess diverted to a beam dump. The resulting laser power, 3-30 W, was sufficient for this series of experiments. Laser powers from 5-22.5 W were evaluated. It was found that 15 W produced the best deposit when used at a scan speed of 1000 μm/s. Decreasing scan speed necessitated a decrease in power. The deposition rate is extremely low below 5 W causing the necessary scan rate to approach zero. A scan rate of 50 μm/s for instance, can have controlled growth at 9 W.

Additional parameters considered in these studies, include level of focus or defocus, and deposition pattern geometry. When making a SALD deposition the laser focus will change as the deposition builds. The higher the structure formed, the more out of focus the laser will be. The Rayleigh length of the laser and lens system used in these studies, defined by: $Z_R = (\pi w_o^2)/ \lambda$ where w_o is the beam waist radius and lambda is the wavelength is 7.3 mm. The defocuses used in this study were from 0.0 to -2.0 mm. It was possible to perform multiple layer depositions without refocusing as the deposit becomes thicker. In some test cases depositions as tall as 1 cm were grown from the substrate before the defocus was to great to support further growth.

The geometric configuration of the deposits was also varied. In many cases an arbitrary rectangular shape was chosen as the deposition pattern; however, when joining tests were performed the rectangle was defined by the plan view of the abutting beveled faces. The raster patterns used were rectangular with alternating long and short sections. The length of the short sections defines the line spacing of the longer dimension. Line spacings of 2.5-50 microns were used in these deposition experiments. Line spacing of 50 μm introduced periodic voids into the deposition. Progressively closer spacing was used to minimize this and to decrease the presence of undesired phases. All joining was performed with a 2.5 micron line spacing. With the rectangular joint fill it is possible to make the raster in line with the joint axis or perpendicular to it. The deposition of multiple layers was performed by rotating the orientation of subsequent layers by 90 degrees, creating a crosshatch pattern.

Characterization

After two and three dimensional deposition tests were performed for the purpose of optimizing the experimental parameters, simulation joint filling tests were performed. A titanium substrate was machined into a series of parallel triangular grooves. The grooves served as spaces that could be filled with deposited silicon nitride. Titanium was chosen because of its resistance to corrosion in the deposition atmosphere and its dissimilarity to the ceramic of study. Depositions were performed and the samples were cross-sectioned to indicate the extent of the SALD and SALDVI fill. Fig 2 is a SEM micrograph for the conditions described in the figure caption.

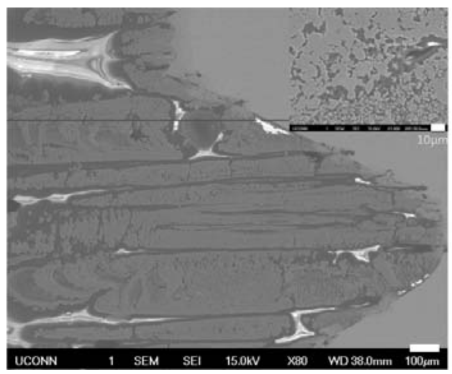
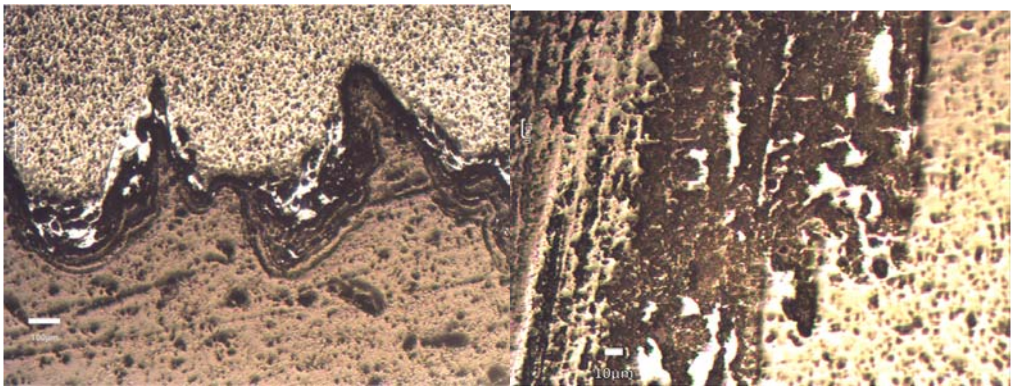


Figure 2: SALD deposit filling a titanium substrate. The laser path from the perspective of this image is from the left to the right. The Experimental parameters were as follows: 15 W focused at the substrate surface with a scan speed of 1000 microns/s; TMS 17 torr, NH_3 45 torr, H_2 160 torr, He 160 torr; line spacing of 50 microns; and four layers of deposition. Image taken by a field emission SEM. The insert is a higher magnification figure taken from the deposit.

The groove fill deposition indicates the potential of the joining process. Cracks formed in the deposited material and some areas indicate porosity. Broad areas of the deposit do not have cracks or porosity and the interface did not show any delamination. A strong continuous interface is very important to the joining process where delamination could be a problem. The interface between the deposited material and the substrate is a chemical and mechanical bonding area. The laser power in this study is such that thermal decomposition occurs as well as substrate ablation. This results in an interface with a greater surface area and a mechanical keying effect.

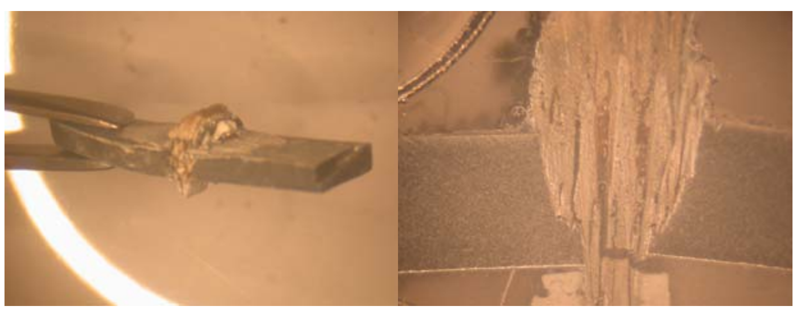


A B

Figure 3. Laser Ablation and Deposition.

The scanned laser creates microscopic grooves in the silicon nitride substrate through ablation when used as the substrate. The left image has a laser incidence direction from bottom to top. The image on the right was taken from a cross section of a joint. The light structure to the right is the substrate and the black and grey structure the deposition. The microstructure at the initial stage, A, is shown to be present in the initial phase of full growth of the deposited joint shown in B. Mechanical keying resulting from the laser/substrate interaction is seen on the beveled surface of the substrate.

The two best silicon nitride joints of this study shared the same gas phase conditions, 20 torr tetramethylsilane, 380-400 torr ammonia, 150 torr H_2, and 150 torr He, which were the optimal pressures. A laser power of 15 W and a spacing of 2.5 microns was used. One of the joints was performed under the SALDVI condition and the other under the SALD condition. The powder used for the vapor infiltration was also silicon nitride. Examples of the two joint are shown below:



A B

Figure 4: Silicon Nitride Joints. Silicon nitride joints of silicon nitride substrates are shown. Image A above shows a perspective view of a silicon nitride joint where vapor infiltration was used. The substrates were resting on the surface of a powder dish, with powder loosely packed into the joint cavity. Image B is a cross section of the silicon nitride joint that did not utilize vapor infiltration. The work piece surfaces attached to the joint appear curved though were flat before deposition, the curvature is an effect of the laser ablation/deposition process. The excess material was not removed.

The silicon nitride SALDVI joint above had less porosity and fewer cracks. Fracture of the joint did not occur at the interface but in the deposit.

Chemical and crystallographic analysis indicates the presence of Silicon Nitride as the major phase in these joints. X-ray diffraction was performed on all deposition samples. Below is an X-ray diffraction pattern corresponding to the deposition conditions above.

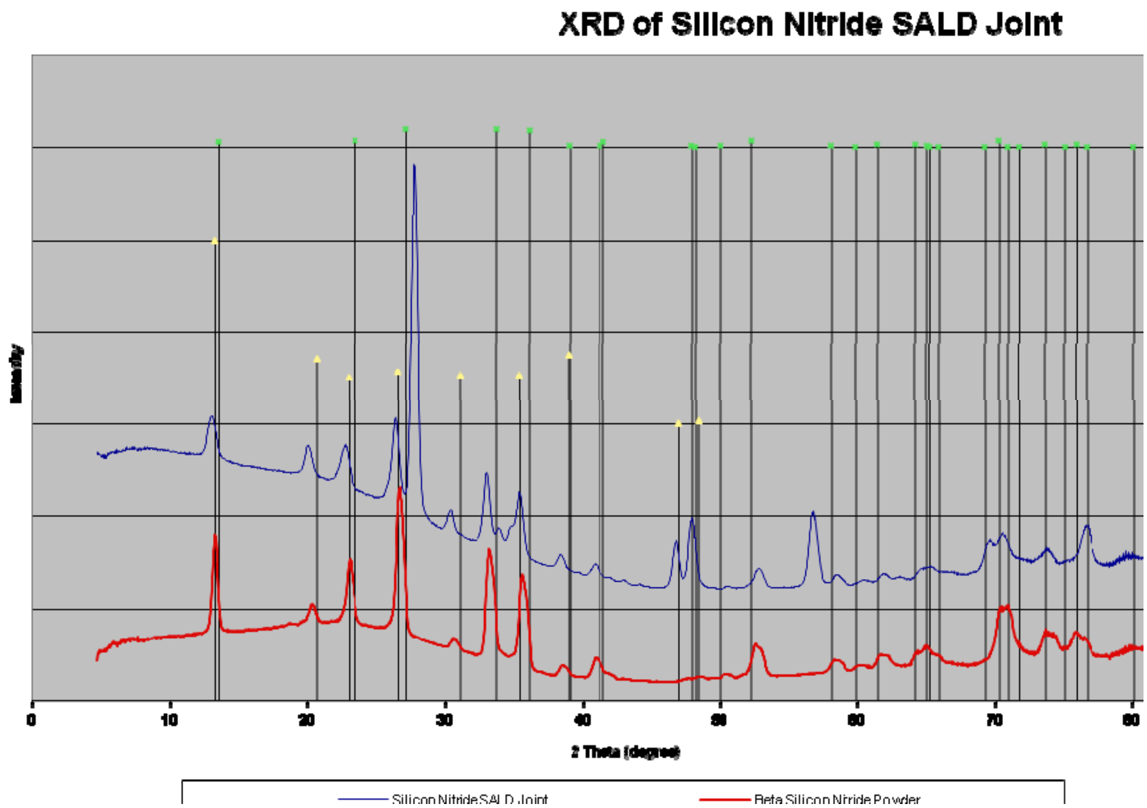


Figure 5: X-ray diffraction pattern of deposited joint material compared to X-ray pattern cards and known Si_3N_4 beta phase powder indicating the deposit is primarily Si_3N_4.

Conclusions

The joining of silicon nitride substrates with locally deposited silicon nitride is demonstrated. The SALD and SALDVI processes can create compositionally appropriate ceramic joints with good substrate/deposit cohesion, augmented by mechanical keying. The process of localized chemical vapor deposition can be taken beyond the application the construction of arbitrary shapes. It is possible to join and consequently repair existing ceramic components. Joint density could be improved through further optimization of the experimental parameters but this type of joining is feasible.

Acknowledgements

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