

Al₂O₃ Precursor Evaluation for SALD Joining

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Abstract:

SFF technology is not limited to the creation of components and objects. Freeform technology can be a mechanism for joining of materials. By defining the space between two objects as the boundary for a free-form object it is possible to form a three dimensional joint fill. Selective Area Laser Deposition or SALD, has been used for free form and joining of carbides and nitrides but has the potential to make other classes of ceramics. By selecting a metal-organic precursor and an oxidizer, an oxide can be created by CVD gas decomposition. In this study such oxide joint fill precursors are studied, particularly for alumina.

Background:

Gas phase laser chemical vapor deposition has been used for the formation of solid freeform objects.[1,2] The technology for Selective Area laser deposition or SALD and Selective area laser deposition and vapor infiltration, SALDVI can be modified for the purpose of joint formation and crack repair. In order to do this the crack or open space of the joint is defined as the inverse of a solid free form object and a computer scan path is generated for the laser. This technique has been used for the formation of silicon carbide joints of tubes in the SALD mode.[3,4,5] Joining attempts were made for flat plate specimens using the SALDVI method.[6] Silicon carbide and Silicon Nitride have been previously explored as the SALD joint fill material but oxides have not. Joining of aluminum oxide using SALD or SALDVI has not previously been reported. Al₂O₃ deposited from the gas phase, is a material that is showing potential as a possible joint fill material, and precursors are being evaluated for this type of deposition.

In order to deposit alumina onto alumina or onto another substrate with the SALD, or SALDVI process, a precursor must be selected. When performing a SiC deposition it is possible to utilize a precursor that, in one molecule, contains the Si and C needed to form the SiC. Tetramethylsilane (TMS) is such a precursor. Other ceramics will often require the use of multiple precursor chemicals. For instance, Si₃N₄ can be deposited with a combination of TMS and ammonia as a nitrogen source. In order to join alumina, a precursor must be selected that contains both oxygen and aluminum, or multiple precursors must be used. Besides this consideration, a viable precursor for the SALDVI process applied to joining should be one with a relatively high vapor pressure. This usually limits the selection candidates to a liquid or gas.

For formation of alumina, several solid precursors exist and have been used in the formation of films but their use necessitates heating for vaporization. They are then primarily used in flowing system hot or cold walled CVD reactors.[7] For deposition using an unheated chamber with a fixed gas supply, this type of precursor is not suitable. Trimethylaluminum (TMA), (CH₃)₃Al was chosen as a source of aluminum because of its vapor pressure, 11 torr at room temperature; it is a liquid at room temperature. TMA has been used in several studies as

the Al source for alumina in certain types of chemical vapor deposition, particularly epitaxial monolayer growth. Although this type of growth is not suitable for the SALDVI process, the experiments indicate alumina is formed with this chemical precursor. The studies also indicate several oxidizer choices. Oxygen sources that have been used for Al₂O₃ growth include, N₂O, NO₂, H₂O and H₂O₂. [8,9] Oxygen was not used in these studies because of the spontaneity of the reaction.

TMA is pyrophoric alkyl and will react immediately with atmospheric oxygen if released. This necessitates special handling and experimental restrictions. In order to use this chemical for deposition studies, the vapor is extracted into a vacuum and the liquid is never exposed to atmosphere or directly to any process oxygen. The TMA is used only below its room temperature vapor pressure to prevent condensation on the chamber walls as a liquid. N₂O or H₂O were chosen as the first precursor possibilities. N₂O as it is a non-toxic gas that can be easily introduced at any pressure. H₂O was chosen because of its stoichiometric reaction potential: $3(\text{H}_2\text{O}) + 2((\text{CH}_3)_3\text{Al}) \Rightarrow \text{Al}_2\text{O}_3 + 6(\text{CH}_4)$. Hydrogen is also added to this reaction though it is not stoichiometrically necessary. Hydrogen in excess, it is believed, assists in the formation of the desired CH₄ product instead of creating hydrocarbon contamination. [10]

Experimental Setup:

The experimental setup for the formation of Al₂O₃ joint is a modified version of the SALD system. A manifold of gasses, Argon, H₂, N₂O and O₂ is attached to the system. The TMA and water are each uniquely valved off from the main system. The TMA feeds into a chamber that serves as a reservoir of vapor so that the TMA liquid does not contact the process gasses. There is a similar chamber for water vapor to prevent the TMA vapor from coming in contact with the liquid water. When introducing the precursors into the system it is desirable to introduce them in the vapor form. The sample work stage is within a vacuum chamber with a window for the introduction of the laser beam. The laser is moved externally by a computer controlled X-Y stage. The laser used in this study is a 1070nm wavelength fiber laser that is CW up to 100 watts. The laser is operated with a 70% beam planar beam splitter as there is instability below 10 watts. With the filter the laser is precisely controllable between 3 and 30 watts. The laser power and stage motion are controlled with a custom National Instruments Labview Code. This code is capable of interpolating a three dimensional machine path, either directly imputed or from a CAD file. The experimental setup is shown in figure 1.

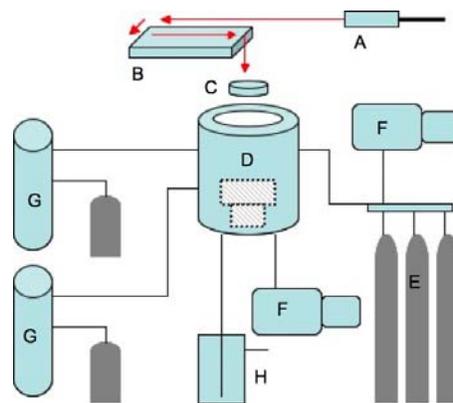


Figure 1: Schematic of Deposition and Joining Setup. A) Fiber laser 1070nm B) X-Y Stage with optical train C) Focusing Lens D) Reaction Chamber E) Gas Cylinders and Manifold F) Vacuum Pumps G) Liquid Precursor and Expansion Chamber H) Chemical Neutralizing Bubbler

The experimental procedure for the determination of viable precursors is as follows. The reaction chamber and expansion chambers are flushed with argon and evacuated multiple times and a 50 mtorr or lower vacuum is established. The reaction chamber and one expansion chamber are filled with TMA vapor and then evacuated to one torr below vapor pressure, vapor pressure being approximately 11 Torr. If water is to be used as the oxidizer the second expansion chamber is filled with water vapor. The partial pressures within the expansion chambers are regulated to achieve the correct ratios upon mixing. Expansion chambers are used so that no liquid, H₂O, H₂O₂, or TMA, can come in contact with a gas with which it might react. The liquids are thus mixed only in the gas phase. Once these precursors are mixed in the gas phase, additional process gasses are added. The gasses, which may be introduced into, the current set up include: hydrogen, argon, nitrous oxide, oxygen, and ammonia. Each gas is introduced through a manifold that has been evacuated so that each gas quantity is controlled.

The purpose of these studies is to ascertain an oxidizer and aluminum source that can be used for pyrolytic laser CVD. A deposition is desired that will match the substrate composition, achieve a high degree of density, and show good adhesive properties to the substrate. Oxygen is not listed as a potential precursor to be used with TMA, since it reacts spontaneously. In order to test oxygen as a potential precursor, two torr O₂ was introduced into a chamber with TMA at vapor pressure. Low oxygen partial pressure was tested for the purpose of finding a lower limit below which, a spontaneous reaction would be prevented or slowed to a negligible pace. Even at this low partial pressure the O₂ rapidly reacted without any heat input from the laser. Below 2 torr the theoretical yield of Al₂O₃ would be too low. A fine alumina powder, which stayed suspended in the air for several minutes, was created by this reaction as well as potentially other byproducts. Studies indicate the reaction: $[(CH_3)_3Al]_2 + O_2 \Rightarrow 2(CH_3)_2AlOCH_3$ [11] may occur.

Results:

Water vapor and N₂O have both been used as oxidizer sources with TMA. Water vapor and TMA will react to form amorphous Alumina, tested by EDS and X-ray diffraction, if the reaction occurs as a liquid based reaction. This was tested by using an over pressure of H₂O and TMA, achieved by heating both liquids so that their vapor pressures would be doubled and allowing this super saturation to mix as a gas. The resulting reaction occurred both within the gas phase and on the surface of the reaction chamber, depositing Al₂O₃ on all cold surfaces and constriction points. When the water and TMA were maintained 1 torr below their vapor pressures the spontaneous reaction either did not proceed or proceeded at a very slow rate.

Nitrous oxide did not react spontaneously with the TMA at room temperature at any partial pressure of N₂O. Gas combinations of TMA, hydrogen and a single oxidizer source, either N₂O or H₂O did not yield a controlled deposition. By combining N₂O and H₂O with hydrogen, argon, and TMA, both SALD and SALDVI deposits were then possible.

Using TMA as the aluminum source, and the combined oxidizer phase of H₂O and N₂O, alumina deposits were formed, both as a deposition into a powder bed and a deposition onto a substrate both alumina. The SALDVI deposition occurred within an alumina powder bed. The bed was created by repeated powder placement, agitation, and flattening by metal scraper. The powder surface was placed at the focal distance of the primary lens. A laser power of 15 watts, CW, was used to create a 3 mm square raster pattern with 50-micron spacing between raster lines. The focused spot diameter at the powder surface was 100 micron. The laser scan speed was 25 microns/s. The TMA and water vapor were used slightly below their vapor pressures. Argon, Hydrogen and N₂O were all added at 150 torr. EDS performed on these deposits confirms aluminum and oxygen ratios of matrix and powder regions of deposit that closely approximate Al₂O₃. X-ray diffraction indicates alumina. The resulting deposition is seen below in the ESEM micrograph, Figure 2:

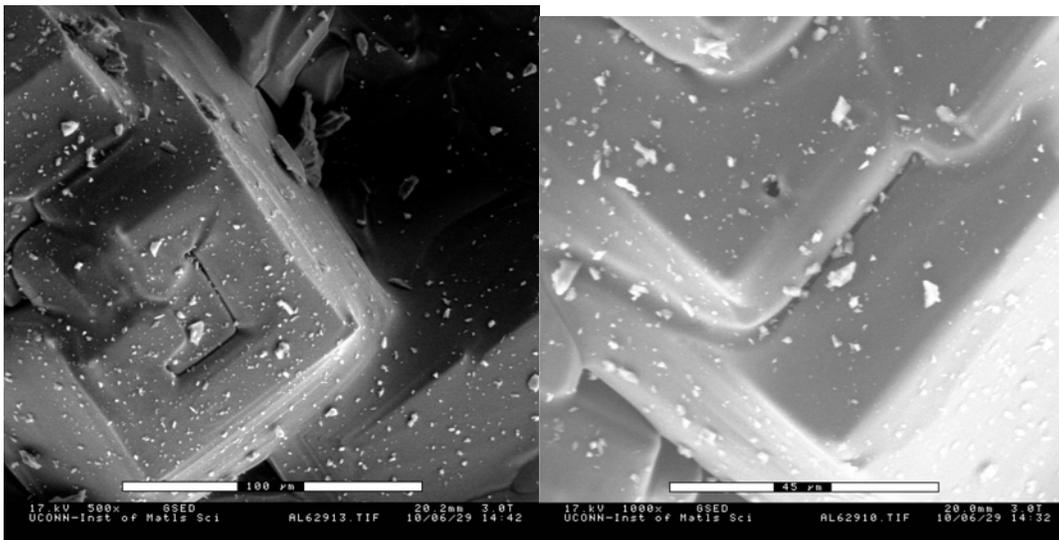


Figure 2: 500x and 1000x ESEM micrographs of SALDVI deposition of alumina into an alumina powder bed. Note the particles imbedded within the deposited matrix.

The SALDVI deposit above appeared dense and was approximately the expected deposition geometry. Metallographic examination is in progress.

Deposition of the SALD type was also performed onto an alumina substrate. The conditions for deposition were the same as above except the raster pattern defined a 1cm x 2 mm scan area and the laser passed each spot 6 passes as apposed to four of powder bed deposition. A deposition was formed with a crisp interface as seen below in figure 3:

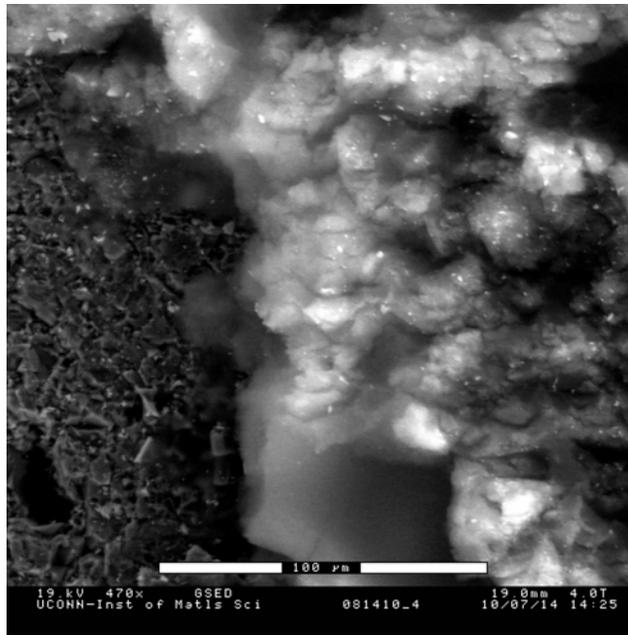


Figure 3: SALD type deposition of alumina (right) on a sintered alumina substrate (left) at 470X magnification

The deposition was a distinctly different from the substrate but failed to achieve the desired density. The deposition did show very good adhesion to the substrate. X-ray diffraction patterns of the above substrate and deposition are shown below in figure 4 as well as an alumina pattern, which closely matches both materials.

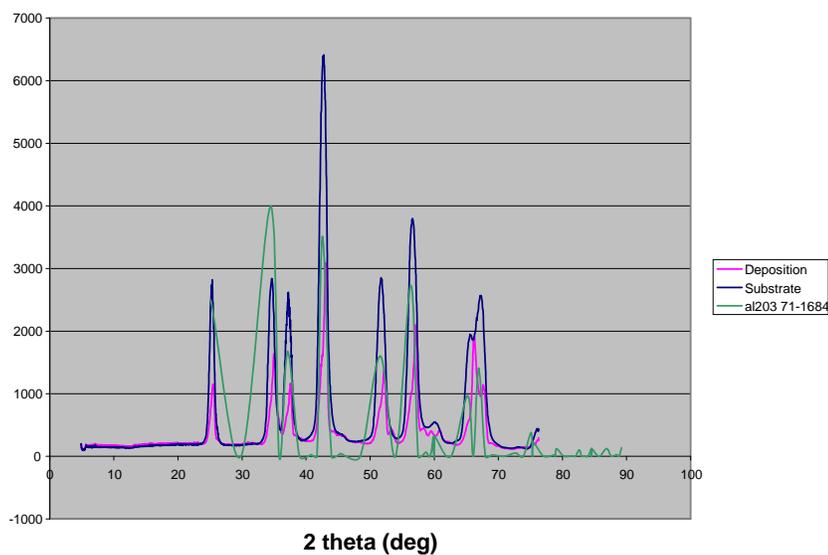


Figure 4: X-ray diffraction patterns of substrate, deposition and corresponding pattern from card 71-1684 alumina.

In an initial SALDVI joint attempt was performed that resulted in a deposition into powder and adhesion to one work piece face. The deposition was composed of only two laser raster passes and consequently resulted in a non dense deposit. Seen below in figure 5 is a deposit on a joint wall.

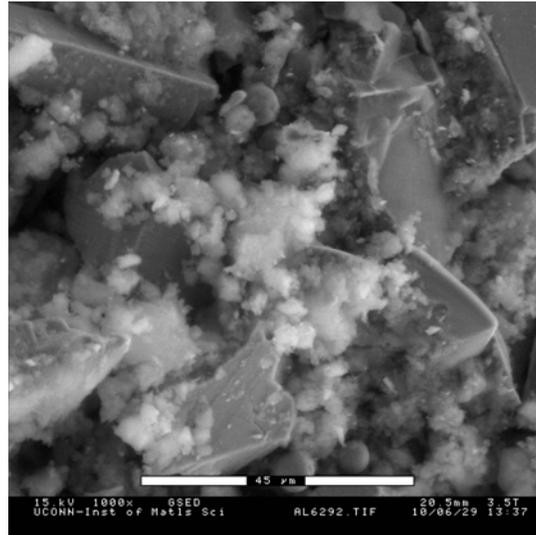


Figure 5: ESEM micrograph of SALDVI type deposit joint fill material. The light fluffy region comprises the deposited material and the larger crystalline shards are powder that has been infiltrated. The base substrate is not seen in this image.

Summary:

Alumina Deposits were successfully made by combining the precursors of trimethylaluminum, nitrous oxide, hydrogen and water vapor. It was possible to use a computer defined laser path to make a deposit of the same geometry. The deposits were well adhered to the substrates. Shorter laser exposure time, resulting from fewer laser passes, resulted in deposits that were not dense. The density and adhesion increased with increasing laser dwell time.

As a precursor for the aluminum component, TMA has potential. A combination of H₂O and N₂O serves as an oxygen source, however, the exact nature of the reaction is not known. There are difficulties in densification and localization of the reaction to the substrate or powder surface; compositionally the alumina is as desired. As these conditions are improved, then joining will be possible with the SALDVI technique for alumina substrates. Work in the area of joining is ongoing which is taking advantage of this precursor selection evaluation.

References:

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