

Rapid Prototyping of Titanium Nitride Using Three-Dimensional Laser Chemical Vapor Deposition

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Selective vapor deposition of titanium nitride was realized from titanium tetrakis-dimethylamide, $Ti(N(CH_3)_2)_4$, at pressures up to 138 mbar. High-aspect-ratio needles up to 12 mm long were grown at axial rates up to 10 $\mu\text{m/s}$. The morphology and composition of the fibers will be described. The temperature rise during transient growth was apparent in the grain size of the resulting needles. Severe mass-transport limitations were also observed due to the multiplicity of precursor by-products. A primary application of this work will be the rapid prototyping of highly-elastic, lightweight structural elements and matrices.

Keywords: Laser Deposition, Titanium Nitride, Fibers, Freeform Growth, Micro-electromechanical Systems.

I. Introduction

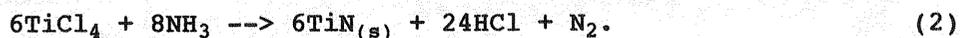
For the *micro-scale* rapid prototyping of metals and ceramics, interest is growing in three-dimensional laser chemical vapor deposition (3D-LCVD). This process employs a laser to deposit solids through the thermal decomposition of organometallic or metal halide vapors, termed *precursors*. A variety of materials may be deposited via 3D-LCVD, including most transition metals,¹⁻⁸ refractory metals,⁹⁻¹¹ and alloys of the same.¹² As demonstrated in a companion paper,¹³ intermetallics may also be grown freely without self-limiting effects. This work represents a first-attempt at depositing another intermetallic, titanium nitride, from the vapor phase.

There have been many attempts to laser-deposit thin TiN films, due to its importance as a diffusion barrier material in microelectronics and as an excellent coating material for wear and abrasion resistance; a variety of precursors have been explored in these attempts. Hopfe et al. produced TiN films, using a mixture of $TiCl_4$, N_2 , and H_2 .¹⁴ The overall reaction was:



In this case, fine-grained TiN films were produced at axial deposition rates of up to 0.2 $\mu\text{m/s}$. In another experiment, Conde et al. grew a 30 μm thick TiN film on Incoloy, with an average axial deposition rate of over 3.7 $\mu\text{m/s}$.¹⁵ Here, the total chamber pressure was 275 mbar, with a $TiCl_4$ partial pressure of 9.3 mbar, the balance of the gas mixture being a 1:1 ratio of N_2 to H_2 . Even more impressive results were obtained on mild steel using a similar gas mixture.¹⁶ In this case, the laser beam was scanned at 4000 $\mu\text{m/s}$, resulting in a 3 μm thick film. The inferred axial deposition rate was 8.6 $\mu\text{m/s}$. Other authors have reported similar axial rates of up to 3.5 $\mu\text{m/s}$.¹⁷

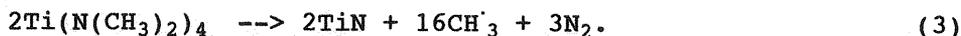
An alternate precursor set for TiN deposition is a mixture of titanium tetrachloride and ammonia, with the reaction:



When this precursor was attempted,¹⁷ solid ammonia-titanium-chloride by-products formed on the substrate and laser windows, making it difficult to produce consistent films. To reduce

the formation of solid by-products, a high concentration of H₂ may be added to the gas mixture, and the gas mixture and chamber should be preheated.

Finally, two additional titanium precursors have been suggested in the literature. The first is titanium tetrakis-dimethylamide, Ti(N(CH₃)₂)₄,¹⁸ which, at low temperatures, decomposes as follows:



At temperatures over approximately 1000°C, the CH₃ ligands dissociate as well, leading to carbon contamination in the deposit. Ti(N(CH₃)₂)₄ may also be mixed with ammonia gas, which tends to prevent the inclusion of carbon.¹⁷

The second precursor, titanium tetrakis-diethylamide, Ti(N(C₂H₅)₂)₄,¹⁹ is more volatile than its dimethyl- counterpart, but has yet to be used in a laser-induced deposition process. In this paper, preliminary results will be presented on the three-dimensional growth of TiN from pure titanium tetrakis-dimethylamide, leaving its mixture with ammonia, and the potential use of Ti(N(C₂H₅)₂)₄ for future papers.

II. Experimental

The apparatus which was used for the TiN experiments is illustrated in Fig. 1. The precursor gases were evaporated into the chamber (A) by heating a source cylinder (B), or by direct connection to a gas cylinder/regulator. The chamber was uniformly heated to a temperature 10-15°C higher than the source cylinder to prevent condensation of the gases within the chamber; in this way, the precursor partial pressure was always determined by the temperature of the source cylinder. Since titanium tetrakis-dimethylamide has a vapor pressure of only 1.3 mbar at 55°C, the precursor was heated in the source cylinder to temperatures over 125°C, yielding Ti(N(CH₃)₂)₄ pressures to 138 mbar. Higher Ti(N(CH₃)₂)₄ partial pressures were not possible, as the precursor decomposes above 150°C, so the chamber temperature had to be maintained at less than 140°C.

The titanium substrate (C) was rigidly affixed to the chamber, through a detachable sample holder (D) which could be placed directly into a scanning electron microscope. The reactor consisted of a spherical cube with six 1.33" CF ports; two ports served as windows for observation and illumination of the sample, while a third port acted as the laser window (E). Each window was heated with a hot air gun (F) to prevent fogging during growth. The fourth chamber port fed a heated nozzle (G) into the chamber from the source cylinder, while the fifth connected the chamber to a cold trap (H) and rotary pump (I), via a flexible bellows (J). The chamber and source cylinder rode on micrometer-driven X-Y-Z stages (K), allowing the sample to be positioned relative to the laser focus. Throughout the experiment, a Lee Laser Nd:YAG laser (10 W TEM₀₀) was employed at 1064 nm. The cw beam was focused with a 90 mm gradient-index lens (L), yielding a 1/e² spot size of approximately 50 microns.

III. Results

Rapid growth of grey-green fibers was possible using the Ti(N(CH₃)₂)₄ precursor at a variety of precursor pressures and laser powers. The color of the deposit indicates that a TiN_xC_y phase, rather than pure TiN was obtained. TiN_xC_y fibers up to 12 mm in length were grown *without focal tracking*, yet with length-to-width aspect ratios as high as 24:1. Typical fiber diameters were on the order of 500-1,000 μm, while in one case, the fiber diameter exceeded 1.3 mm. These diameters

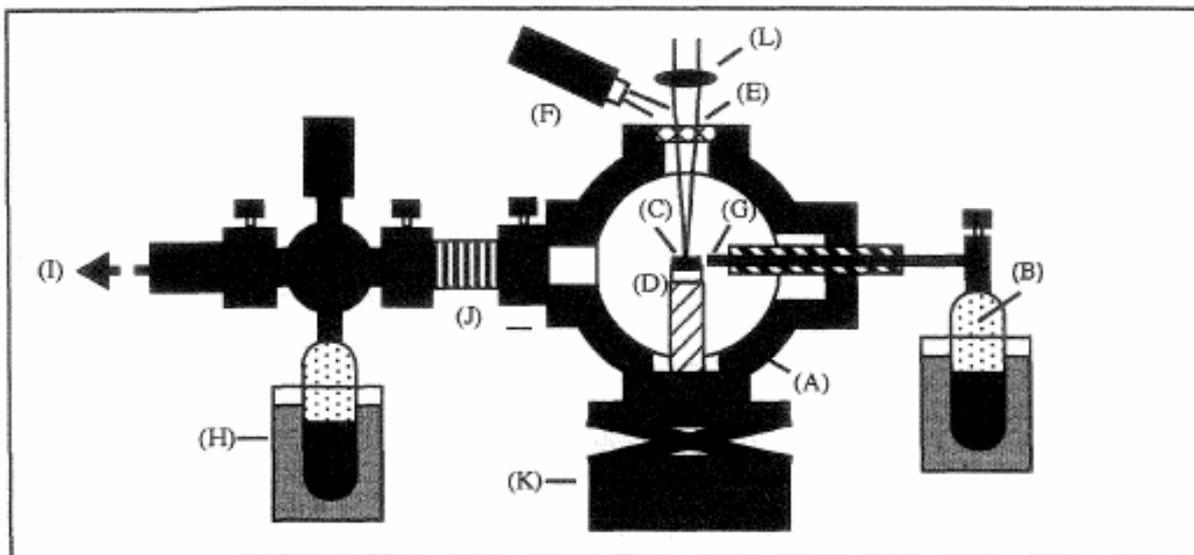


Fig. 1: Experimental Apparatus for the TiN Experiments

are large compared with most laser-deposited materials,²⁰ and are caused by the high thermal conductivity of TiN_xC_y (approx. 0.08 cal/s-cm-K), which tends to broaden the reaction zone—allowing conduction down the rod, so that continued growth occurs far from the rod tip. The initial (transient) diameter of the fibers was comparable to (or slightly less than) that of the steady-state fiber diameters, with a very short transient growth period. This is due to the low threshold decomposition temperature of the precursor, combined with the higher thermoconductivity of the TiN deposit (0.080 cal/s-cm-K) relative to that of the Ti substrate (0.05 cal/s-cm-K). Similar transient results were obtained in the growth of iron and nickel rods on alumina and graphite sheets.¹² Interestingly, the steady-state diameter of the TiN_xC_y rods narrowed with rising laser power, perhaps due to the decreasing thermoconductivity of TiN_xC_y with temperature.

A wide variety of laser powers were employed, from 0.60 W to 10 W . No significant growth was observed below 2.0 W , while at the threshold power of 2.1 W , rods could be readily grown at rates of $2\text{-}3 \mu\text{m/s}$, such as those shown in Fig. 2. The reaction rate was mass-transport limited, with increased natural convection observed at the highest laser powers (by monitoring particulate motions in the precursor gas). Growth rates rose slowly with laser power, reaching a maximum of $10 \mu\text{m/s}$ at 7.9 W . This growth rate is excellent for such low precursor pressures. Clearly, the multiplicity of by-products, coupled with a $\text{Ti}(\text{N}(\text{CH}_3)_2)_4$ mass-diffusivity approximately $1/15\text{th}$ that of hydrogen, gave rise to convection cells even at low pressures—enhancing the average fiber growth rate.

At the highest powers, the deposition rate became erratic, no growth being observed at powers between $9\text{-}10 \text{ W}$. This phenomenon has been previously observed in the growth of nickel rods,²¹ and may be explained in two possible ways. If the reaction is endothermic, the rate may be thermodynamically-limited at excessive temperatures. Second, since there is a high Stefan flow, for every precursor molecule which decomposes, a plume of by-products builds up in the center of the rod where the temperature is the highest, and the reaction is starved at the center. This was clearly seen in SEM photos of the TiN_xC_y fibers, where all of the rods have a central depression. In several cases, the fibers were completely hollow!

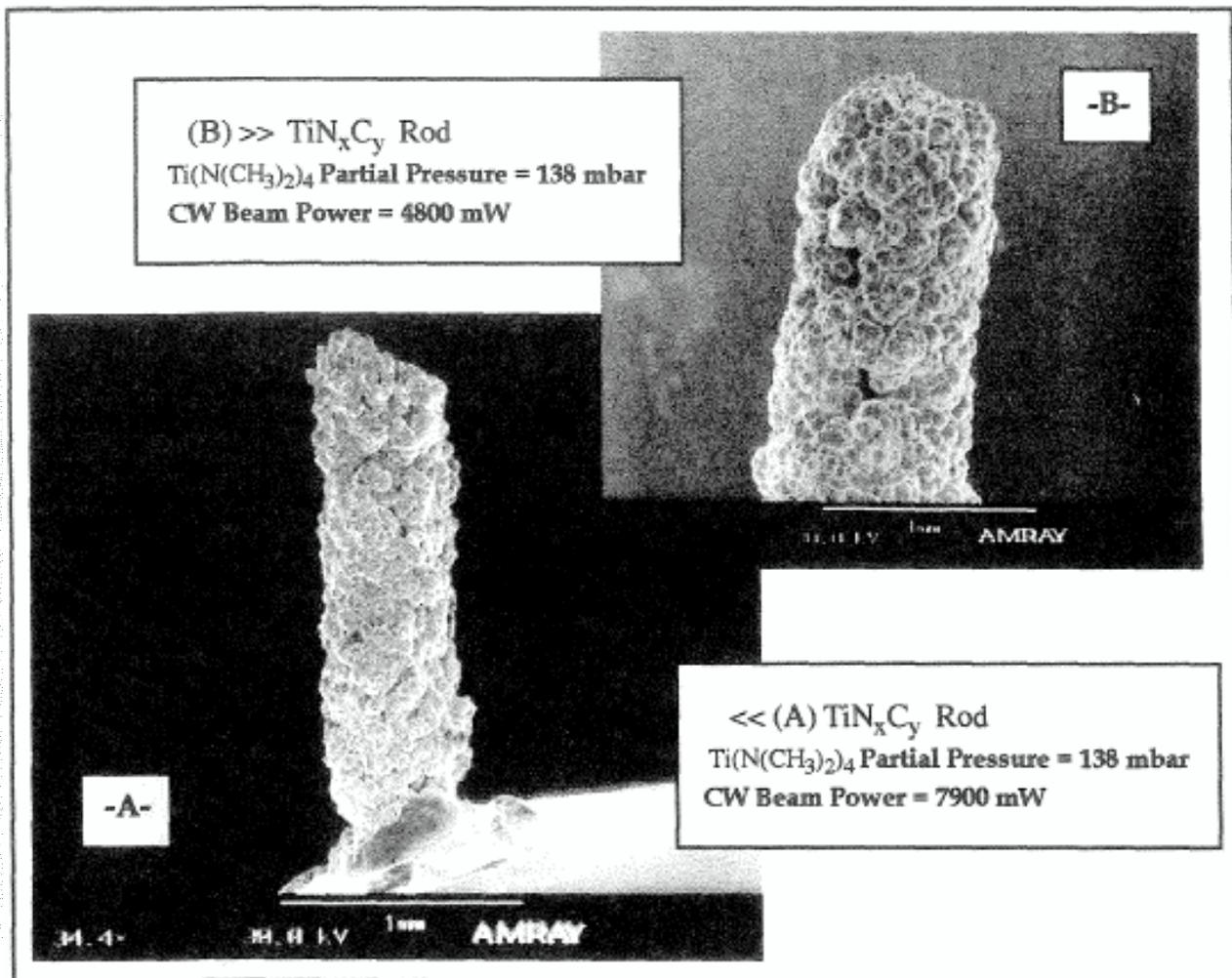


Fig. 2: Three-dimensional Titanium Nitride Growth

The steady-state grain size of the deposit varied markedly with laser power, in some cases reaching over $100\ \mu\text{m}$. Large grain sizes are to be expected for TiN_xC_y at low precursor pressures, because of the simple cubic structure of TiN and TiC. As can be seen in Fig. 2, the grain size also increased rapidly over the transient growth regime—indicating a rapid rise in temperature with distance from the Ti substrate. Yellow-white emissions were observed during all of the steady-state growth experiments, indicating a high deposition temperature, probably in excess of 1000°C .

Several methods are being investigated to measure and control the temperature during growth, so that high-strength fibers of fine grain structure may be grown. The addition of inert gases, such as xenon or krypton, is being investigated as a means to cool the fibers during the steady-state regime, and active feedback control of the peak reaction temperature will be possible through a simple temperature measurement apparatus.¹³

At most laser powers, solid by-products were generated readily in the gas-phase, and coated the laser window and chamber walls. This grey-green powder was also TiN_xC_y , but with high concentrations of carbon—again indicating that the reaction temperatures were greater than 1000°C . In addition, the powder formed freely away from the substrate or deposit, so some photolysis of the precursor was apparent. To avoid this phenomenon, efforts are underway to determine the absorption spectrum of $\text{Ti}(\text{N}(\text{CH}_3)_2)_4$ and employ alternate laser wavelengths.

IV. Conclusions

While $\text{Ti}(\text{N}(\text{CH}_3)_2)_4$ holds promise as a precursor for micro-scale rapid prototyping of TiN, the deposition rate is limited by the maximum vapor pressure which can be attained before decomposition of the precursor occurs. The exact composition of the TiN_xC_y deposit is presently under investigation using glow discharge optical spectroscopy; however, the deposits appear to be contaminated with carbon, indicating decomposition of the CH_3 groups. To eliminate this contamination, high pressures of ammonia and hydrogen will be attempted with this precursor, as well as the addition of noble gases to cool the reaction. Active control of the temperature may also be necessary to obtain fine-grained deposits. To achieve the rapid TiN growth rates which would be appropriate for large-scale prototyping ($>100 \mu\text{m/s}$), however, an alternate precursor should be selected.

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