Solid Freeform Fabrication of Silicon Nitride Shapes by Selective Laser Reaction Sintering (SLRS)

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Abstract

Selective Laser Reaction Sintering is a variation of selective laser sintering (SLS) that incorporates an in-situ reaction under the scanned beam to fabricate shapes from materials not directly accessible by traditional SLS. This paper describes an investigation into the production of silicon nitride (Si_3N_4) shapes by laser sintering silicon powder in an ammonia (NH_3) atmosphere. The effect of gas pressure and the importance of gas/laser interactions are discussed. Single and multiple layer shapes are fabricated. The material is analyzed by x-ray diffraction spectroscopy (XRDS) for phase content and scanning electron microscopy (SEM) for macrostructure. Data is presented that demonstrates conversion rates from silicon to silicon nitride on the order of 85%.

Introduction

Selective Laser Reaction Sintering (SLRS) is a solid freeform fabrication process under development at The University of Texas at Austin that combines selective laser sintering (SLS) technology and reaction sintering concepts. The process is similar to SLS in that a laser is scanned across a powder bed to selectively heat and sinter areas that represent cross sections of the desired shape. Multiple layers of powder are consecutively scanned to build up a three-dimensional shape. The process differs from traditional SLS in that the laser drives both sintering and simultaneous reaction processes under the beam. These reactions can take place between the sintering powder and a reactive atmosphere, gas/powder SLRS, or between different phases in the sintering powder, powder/powder SLRS.

The simultaneous reaction has been incorporated into the process in the attempt to directly produce shapes from ceramic materials that cannot be directly processed by traditional SLS. Traditional SLS requires the formation of a liquid phase for adequate sintering to occur in the very short times at temperature inherent to the scanned beam process. Unfortunately, many desirable ceramic materials either have very high melting points that make liquid phase formation difficult, or they decompose from the solid phase without melting. For example, one of the most commonly used high performance ceramics, alumina (Al_2O_3), melts at 2015° C [1]. Two other high performance ceramics, silicon carbide (SiC) and silicon nitride (Si_3N_4), both decompose before melting, with decomposition temperatures of 2560° C and 1900° C, respectively [2,3]. SLRS may provide the means to laser sinter these 'nonsinterable' materials by using precursor materials that form relatively low melting point intermediate liquid phases under the scanned beam. The liquid phases facilitate the sintering process and subsequently react to form the desired product phase.

Preliminary gas/powder SLRS success has been reported for the production of both Al_2O_3 and SiC shapes [4,5]. The Al_2O_3 shapes were produced by laser sintering aluminum powder in air. The aluminum, with a melting point of 660° C, provided the requisite liquid phase that in turn reacted with oxygen in the air to produce Al_2O_3. The SiC shapes were produced by laser sintering silicon powder in both acetylene and methane gas. In this case, silicon provided the liquid phase with a melting point of 1413° C which in turn reacted with the acetylene or methane precursor to produce SiC.

The purpose of the work described in this paper was to determine if gas/powder SLRS could be used to produce silicon nitride shapes. Conceptually, gas/powder SLRS of Si_3N_4 is performed by laser sintering silicon powder in a nitrogen atmosphere. Liquid silicon produced by the scanned beam reacts with the nitrogen gas during the sintering process to form solid silicon nitride. For this study, gaseous ammonia (NH_3) was used as the nitrogen source instead of diatomic nitrogen (N_2) because it more readily decomposes to produce monatomic nitrogen. It is believed that monatomic nitrogen is required for the nitridation process. The overall reaction was expected to proceed as follows;

$$3Si_{(liquid)} + 4NH_{3(gas)} \rightarrow Si_3N_{4(solid)} + 6H_{2(gas)}$$

The objective was to directly produce a Si_3N_4 shape with total conversion from silicon to silicon nitride occurring under the scanned beam.

Experimental Arrangement

The experimental arrangement used for this work has been previously described in the literature [6]. It consists of a laser scanning system, a miniature SLS style powder delivery system and an environmental chamber. The chamber provides environmental control enabling the sintering process to be performed in both reactive and inert atmospheres. The powder delivery system, which is located inside the chamber, provides multiple layers of powder to a target area. A laser beam is directed onto the target area through a transparent window on the chamber. Scanning is accomplished using a servo driven x-y table that translates the chamber/target area under the static beam. Two lasers are available, a 25 watt cw CO_2 laser (10.5μm-10.7μm wavelength), and a 150 watt cw Nd-YAG laser (1.06μm wavelength) to provide flexibility both in terms of available power and wavelength.

Experimental Results

Single layer tests were performed using -100 mesh (<144μm) silicon powder (99.5% purity) and anhydrous ammonia (NH_3) gas (99.999% purity) precursor materials. Scans were performed using both CO_2 and Nd-YAG lasers. A rectangular scan pattern was used to produce test coupons which were analyzed using powder x-ray diffraction spectroscopy (XRDS) to semi-quantitatively determine phase content. The analysis was performed by comparison of x-ray diffraction patterns taken from powder standards containing silicon and α-Si_3N_4 or β-Si_3N_4 with patterns taken from the test coupons (after grinding) produced by SLRS.

The single layer tests performed using the CO_2 laser were limited to relatively low ammonia pressures (≤ 100 torr) due to absorption of beam energy by the NH_3 gas. The gas absorption of the beam's energy, which is attributed to interactions between the laser's output wavelength and NH_3's molecular vibration modes, was both severe and nonuniform. The nonuniformity in absorption was attributed to laser mode hopping (changes in the unstabilized CO_2 laser's output wavelength) in combination with the fact that ammonia's gas absorption behavior is very wavelength dependent [7]. The result was unacceptable power fluctuations at the substrate surface when using gas pressures greater than 100 torr. These fluctuations can be seen in a gas transmission test performed at 136 torr NH_3 gas pressure, Figure 1. The test was performed by directing the laser beam through a chamber filled with NH_3 gas and measuring the transmitted power over time.

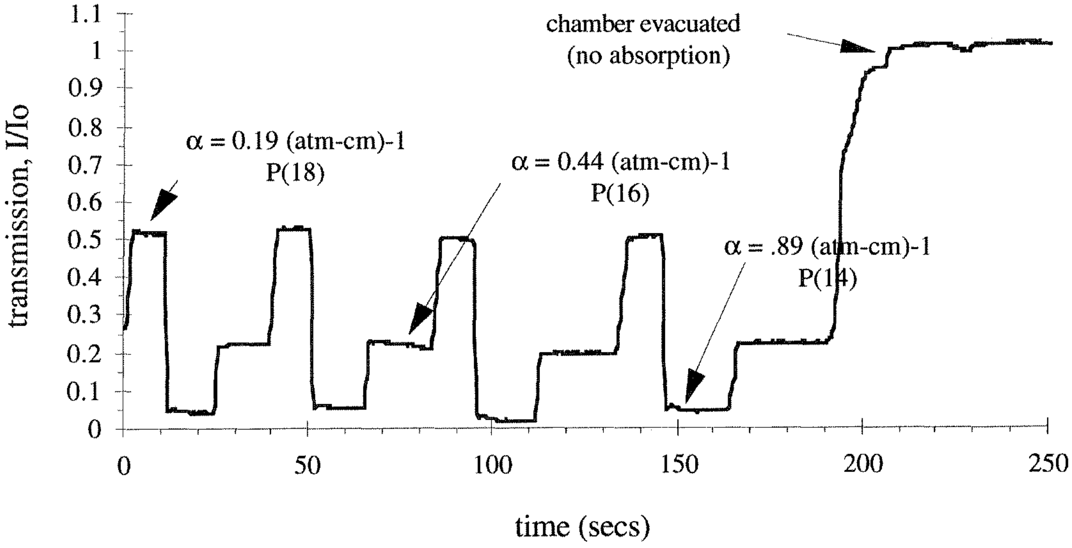

Figure 1: Transmission test, CO_2 laser, 136 torr NH_3, 18cm path length.

Gas absorption coefficients, α, as used in the standard Beer-Lambert relationship below, were determined for the three distinct observed levels of absorption. The coefficient varied from 0.19 to 0.44 to 0.89atm^{-1}cm^{-1}.

$$I = I_0 e^{-\alpha x p}$$

α = absorption coefficient
x = path length, cm
p = gas pressure, atm

Comparison with literature values for absorption coefficients suggests that the CO_2 laser used for this work oscillates between the P18(10.571μm), P16(10.551μm) and P14(10.532μm) output modes(wavelengths) [8].

XRDS performed on test coupons produced using 100 torr NH_3 and the CO_2 laser detected the formation of both alpha and beta forms of Si_3N_4, Figure 2. Comparison with standards indicated that total conversion to Si_3N_4 was approximately 54% by weight.

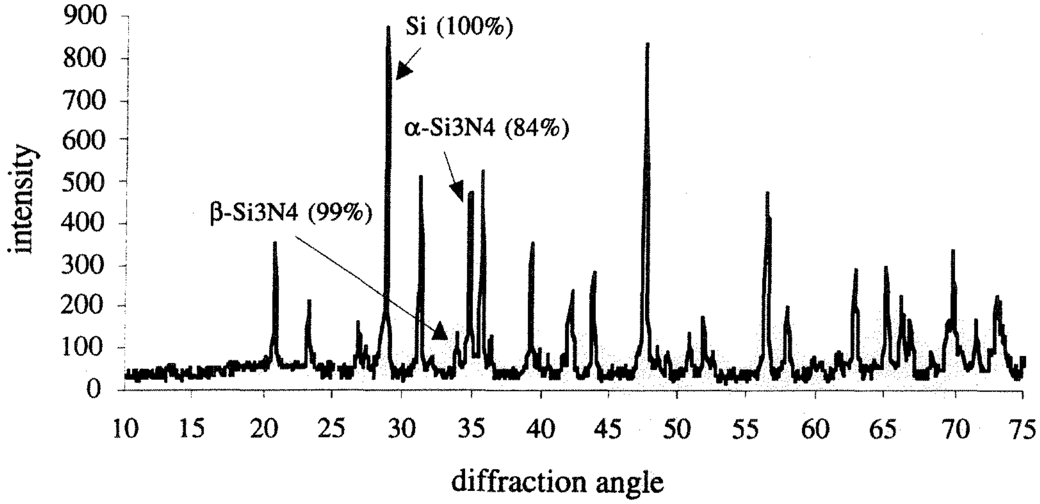

Figure 2: X-ray diffraction spectra from single layer 'Si_3N_4' test coupon made using -100 mesh Si, 100 torr NH_3 and 15 watts CO_2 laser.

In spite of the pressure limitations and incomplete conversion to Si_3N_4, multilayer shapes were made using the CO_2 laser. SEM micrographs taken from a cross section of one of the shapes reveals relatively uniform material and good interlayer bonding, Figure 3.

Note that consecutive layers were made using alternating scan directions. As a result, the cross section is perpendicular to scan direction for the bottom most layer and every other layer thereafter. Shape density was determined to be 0.86 g/cm^3 or approximately 31% theoretical assuming 54 weight % conversion to Si_3N_4.

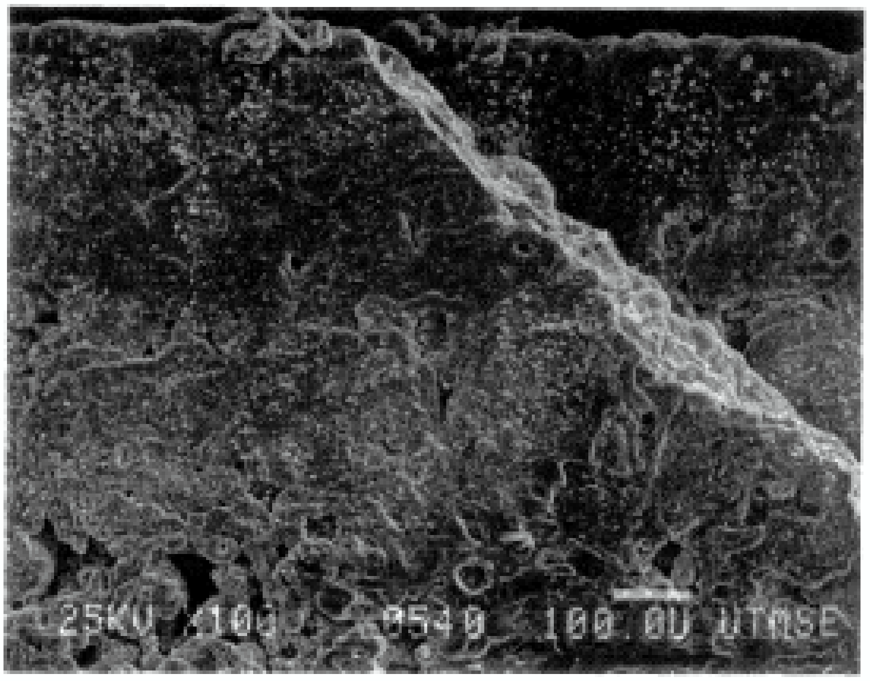

Figure 3: SEM micrograph, cross section of multilayer shape. -100 mesh silicon, 100 torr NH_3, 15wattts CO_2 laser power, 225μm layer thickness.

Single layer tests were also run using a Nd-YAG laser (1.06μm wavelength). Gas absorption tests indicated that NH_3 was transparent to the 1.06μm radiation. This made it possible to produce a series of coupons at increasing pressures to determine the effect of NH_3 pressure on the SLRS process. The coupons were analyzed by XRDS, and the phase content was quantified by comparison with standards. The results, Figure 4, indicate that conversion to nitride increases with increasing pressure. Maximum conversion, 85 weight %, was obtained at the highest NH_3 pressure tested, 700 torr. Note that both alpha and beta Si_3N_4 phases were formed during the process.

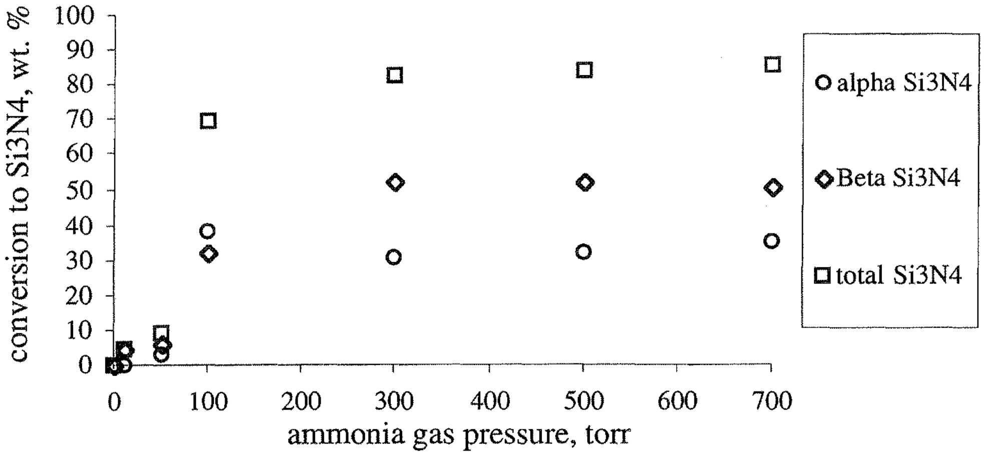

Figure 4: Conversion to Si_3N_4 versus NH_3 pressure, determined by x-ray diffraction.

Multilayer shapes were made using the Nd-YAG laser and 700 torr NH_3. SEM micrographs of a cross section of one of the shapes reveals a porous, nonuniform structure. There are indications of interlayer bonding, and some regions of the shape appear to be relatively dense, Figure 5.

Figure 5: SEM micrograph, cross section of multilayer 'Si_3N_4' shape made using -100 mesh Si, 700 torr NH_3 and 9 watts Nd-YAG laser power.

Discussion

The primary observation to make concerning this work is that large percentages of a silicon powder precursor can be converted to solid silicon nitride directly under a scanned beam. XRDS indicated that by using ammonia as the nitrogen source, 'silicon nitride' shapes could be made containing up to 85 weight % silicon nitride. This degree of conversion was obtained using scan parameters that result in build rates on the order of 1.5 mm^3/min. This translates to production of a 1 cm x 1 cm x 1 cm cube in roughly 10 hours.

Conversion was determined to be a function of precursor pressure, increasing with pressure up to the maximum test pressure of 700 torr. It appears that further increases in precursor pressure will result in even higher conversion rates. Though the work was not presented here, it was also observed that conversion increased with decreasing scan speed and/or decreasing scan spacing. This indicates that gas pressure and scan parameters can be optimized to achieve high conversion rates.

Another observation to make from this work concerns beam interactions with the precursor materials. The severe, nonuniform absorption of CO_2 laser energy by NH_3 gas clearly demonstrated that the laser must be considered as more than an energy source. In this case, the use of an alternative wavelength laser, the Nd-YAG, eliminated the problem. It must be noted that two additional laser interactions, subtrate reflectance and transmission can also be strong functions of laser wavelength, particularly for ceramic materials. These interactions determine how the laser energy is absorbed which in turn strongly affects the resulting temperature distribution that drives the process. As a result, it will be necessary to consider not only the beam interaction with the gas precursor, but also substrate reflection, absorption and transmission of the laser beam to fully optimize the SLRS process.

The multilayer shapes made during this study were made to demonstrate proof-of-concept for the gas/powder SLRS of Si_3N_4. The main objective of the work has been to optimize conversion to Si_3N_4 without consideration as to effect on density and mechanical integrity of the produced shape. To this date, the produced shapes have had low densities and minimal mechanical properties. Future work will look to optimize process parameters, both in terms of conversion and mechanical properties. As mentioned previously, conversion has been shown to be dependent on scan rate, scan spacing and gas pressure. It may be possible to produce a shape having both high conversion and good mechanical properties by manipulating these process variables. It is also believed that thermal stresses induced by the scanned beam have a deleterious effect on the resulting fabricated shape. Work is in progress to develop a heated stage to raise powder bed temperatures. This should reduce temperature gradients developed in the shape during manufacture, thereby reducing thermal stresses.

Summary

'Silicon nitride' shapes containing in excess of 85 weight % Si_3N_4, the remainder being silicon, have been produced directly by the scanned beam SLRS process. Work is ongoing to further increase Si_3N_4 content and begin optimization of the process to improve shape density and mechanical properties.

Acknowledgements

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