# LAMINATED OBJECT MANUFACTURING OF $Si_3N_4$ WITH ENHANCED PROPERTIES

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## ABSTRACT

The potential to fabricate near net-shape ceramic components of intricate shape is attractive and offers considerable savings in cost and time. The laminated architecture inherent in many Rapid Prototyping techniques can be utilized to enhance material properties by providing weak interfaces at regular intervals, oriented microstructures, and functionally graded compositions. By design and control of these variables it is possible to enhance the strength, toughness and performance of components fabricated from structural ceramics. A range of oriented microstructural features have been investigated in Laminated Object Manufacturing of $Si_3N_4$ materials. Changes in the mechanical properties can be related to specific architectures and microstructural developments which took place during sintering.

## INTRODUCTION

The damage-critical material properties of ceramics can be significantly improved through lamination of the structure prior to densification. Building ceramics in this way has been shown to reduce the primary flaw size and introduce a number of interfaces, which if carefully designed can influence the microstructural development and material properties, resulting in materials which exhibit damage tolerance and non-catastrophic failure modes, especially in bending. Lamination is an inherent signature of many Rapid Prototyping techniques and it is a powerful and flexible approach to materials design that can be used to produce a wide range of material structures. In this study, three approaches have been investigated in an attempt to improve the mechanical properties of $Si_3N_4$ laminates for Laminated Object Manufacturing (LOM). The composition of the individual layers was gradually changed to produce functionally graded materials (FGMs),[1,2] primary seed crystals were aligned within each of the layers to achieve a microstructure with a preferred orientation,[3] and the interlaminar composition and microstructure has been changed through the addition of a second phase to introduce non-linear fracture behavior and thereby overcome the inherent brittleness of the materials within the individual layers.[4]

Although several techniques are available from which to fabricate laminated or graded architectures, tape casting followed by lamination has demonstrated excellent control over laminate thickness, scale, and uniformity of properties.[5,6,7,8] In order to obtain optimal properties with the manual lamination of ceramic tapes it is necessary to "heal" the interfaces between the individual tapes via thermocompression, which normally takes place at the softening temperature of the plasticizer (50°C to 100°C), for 10 minutes under a pressure of 30 - 70MPa.[8,9] Thermocompression is essential in manually laminated ceramics where strong interfacial forces are required (i.e., $Al_2O_3$/$Al_2O_3$ and $Al_2O_3$/$ZrO_2$). Although ceramic tapes can be used for Rapid Prototyping through the LOM process, the thermocompression stage is difficult to reproduce. The equivalent, but less effective stage in the LOM process utilizes a hot roller or plate[10] which traverses or rests on the tape, thereby applying a small load (~0.7Mpa) for a much shorter period of time. Additionally, post pressing of the laminated block[11] has been investigated prior to decubing. Although higher loads, temperatures and longer periods of time would be beneficial in promoting bonding between the tapes, increasing these parameters could distort the tapes, leading to shape dependent dimensional changes that are incompatible with the net-shape LOM process. It has therefore been necessary to investigate alternate methods to achieve interlayer adhesion during LOM fabrication of ceramics. Applying a solvent-based solution between layers has demonstrated sufficient adhesion to successfully complete the LOM fabrication process, following which, laminate healing without anisotropic dimensional distortion of the net-shape component can be achieved by isopressing.[12]

Since it is apparent that an interlayer adhesion processing stage is necessary during LOM fabrication of ceramics, this stage has been investigated further to introduce different laminate interface material systems, thereby changing the overall material properties. Selection of the appropriate material systems, layer thickness and interlayer coating (if any), should enable LOM fabrication of components which exhibit damage tolerance and graceful failure similar to that which has been described in the literature for manually laminated systems. The nature of the designed interface between subsequent layers can be broadly classified as weak bonding, strong bonding, or a combination (hybrid bonding) of both of these mechanisms.[4] Typically, weak interfaces have given rise to flaw-tolerant behavior[13,14] through the deflection of cracks and the dissipation of energy along the interface normal to the load. Flaw-tolerance has also been demonstrated in strong interface systems containing two brittle materials,[15] in transformation toughened systems,[6,16] and in systems based on alternating layers of metals, intermetallics or ceramics.[17,18,19] Unless considerable care is taken to ensure otherwise, most components fabricated via the LOM process will exhibit weak interfaces due to uncontrolled interfacial mating of the layers, and residual oriented porosity. Many of the weak interface composites fabricated from $Si_3N_4$/BN,[20,21] $Al_2O_3$/phosphate,[22,23] and SiC/C[13,14] could be applied to components laminated by LOM with resulting improvements to the damage tolerance and component performance.

This paper reports on a materials study in which the compatibility of $Si_3N_4$ tapes with the LOM process was investigated, and three "easy to apply" microstructural variants were evaluated to enhance the properties of multilayer $Si_3N_4$ structures. Specifically, second phase interface compositions, FGMs, and oriented microstructures were studied. Differences in mechanical properties are related to the specific architectures and the microstructures which evolved during sintering. A gas pressure sintering technique, which unlike hot pressing does not create anisotropic dimensional changes that significantly distort the net-shape component, has been investigated and is of particular relevance to the LOM process because it provides controlled or uniform shrinkage during densification.

## EXPERIMENTAL APPROACH AND RESULTS

### *I. Materials Study: Designed Architectures in $Si_3N_4$ Laminates*

Three different laminated architectures were fabricated in an attempt to tailor the microstructure and properties of $Si_3N_4$. Although the materials were manually laminated, the architectures can all be easily applied to the automated LOM process. The source of the $Si_3N_4$ powder and $Y_2O_3$, $Al_2O_3$, and $ZrO_2$ sintering aids is given in Table I. The fabrication process for the laminated $Si_3N_4$ ceramics is illustrated schematically in Figure 1. Powders were ball milled in toluene and ethanol for 24 hours, followed by a further 24 hours with the plasticizer and binders in a proprietary composition. Following blending, the ceramic slips were degassed for two minutes and cast at a speed of 4 cm/sec onto mylar using a 6" blade caster. Casting and drying were carried out at a temperature of between 21°C and 23°C. For all materials, the tapes were cut, stacked, and thermocompressed at a temperature of 70°C and pressure of 14MPa for 10 minutes.

**Table I.** Powder source and composition

| Material | Source | Size (μm) | Purity% |
|---|---|---|---|
| $Si_3N_4$ | UBE SNE10 | ~0.3 | 98.5 |
| $Al_2O_3$ | Baikowski CR125 | <0.2 | >99.99 |
| $Y_2O_3$ | F.J. Brodmann | ~1.0 | >99.99 |
| $ZrO_2$ | Tosoh TZ-3Y | ~0.03 | ~94.8 |

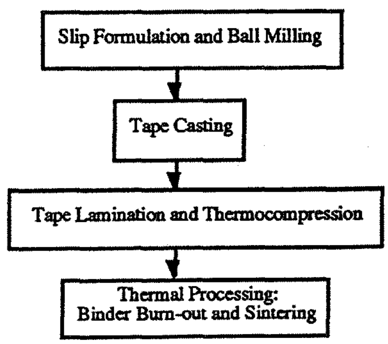


**Figure 1.** Lamination of $Si_3N_4$

Functionally Graded Materials (FGMs)

Functionally graded $Si_3N_4$/SiC laminated structures were fabricated in an attempt to introduce surface compressive stresses resulting from the difference in thermal expansion coefficients between SiC and $Si_3N_4$. For armor applications, the graded architecture allows for the development of a back surface compressive stress that can increase the time to failure of ceramic armor plates while minimizing the impedance mismatch that has caused poor ballistic behavior in non-graded bi-material laminated armor.[24] The $Si_3N_4$/SiC powder mixtures were blended with 5wt% of both $Al_2O_3$ and $Y_2O_3$ as sintering aids, and the process shown in Figure 1 was used to fabricate laminated structures that graded from 50wt% $Si_3N_4$/50wt% SiC in the middle of the structure to 100% $Si_3N_4$ on both surfaces. Grading took place in increments of 10wt% as shown in Figure 2. These materials were hot pressed in a $Si_3N_4$/BN powder bed at 1780°C and 25MPa for two hours. Figure 3 is an optical micrograph of the densified $Si_3N_4$/SiC FGM and Figure 4 is a schematic diagram of the estimated surface compressive forces that are balanced by an internal tensile force. $Si_3N_4$/SiC FGMs containing SiC (Nicalon) continuous fiber reinforcement were also fabricated, but it was observed that even when hot-pressed the introduction of fibers led to poor densification and porosity around the fibers that weakened the structure, resulting in a lower strength and inferior ballistic performance.

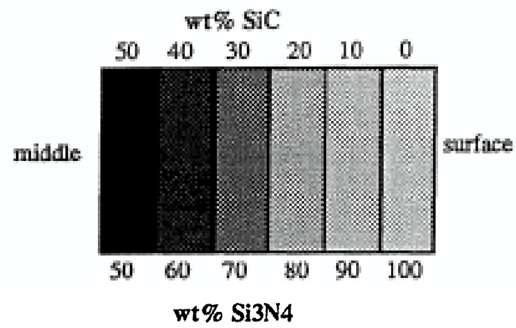

**Figure 2.** Graded $Si_3N_4$/SiC Structure

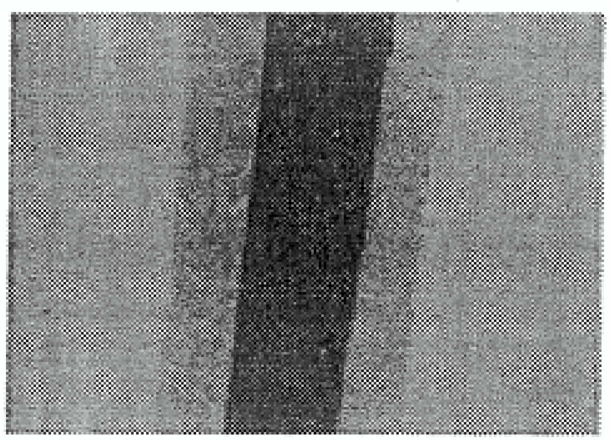
**Figure 3.** Micrograph of Graded $Si_3N_4$/SiC

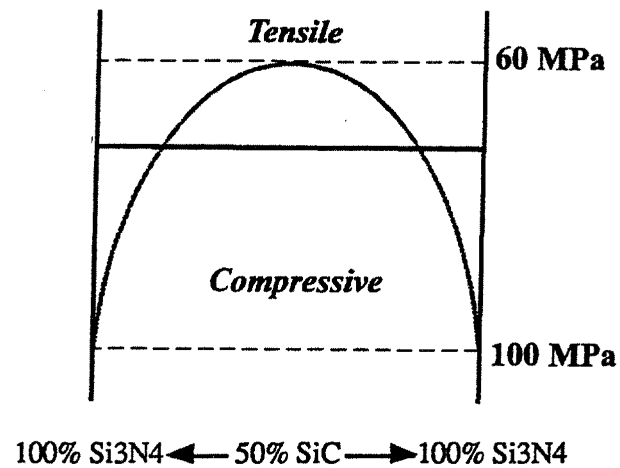

**Figure 4.** Stresses in Graded $Si_3N_4$/SiC

Second Phase Interfacial Design

Investigation of four different laminate interfaces was carried out using $Si_3N_4$ tapes with 5wt% of both $Al_2O_3$ and $Y_2O_3$ as sintering aids. A thin coating of a second phase interface material was applied as a 5wt% solution/suspension in ethanol, by a simple spray technique prior to lamination. The interface materials evaluated were BN, $SiO_2$, $TiO_2/SiO_2$, and SiC (formed in-situ from $SiO_2$ and sugar[25]). These materials, designated as SN-BN, SN-$SiO_2$, SN-$TiO_2/SiO_2$, and SN-SiC, respectively, were hot pressed in a $Si_3N_4$/BN powder bed at 1780°C and 25MPa for two hours.

This study was undertaken to determine if the laminate interface could be tailored to control the fracture behavior of laminated $Si_3N_4$ structures. The BN and $TiO_2/SiO_2$ materials were intended to provide weak interfaces due to the low strength and lubricious characteristics of BN and $TiO_2$, while the SiC and $SiO_2$ materials were intended to provide strong interfaces through efficient load transfer across the interfaces of the laminated $Si_3N_4$ structure. Four-point flexural strength was measured on five specimens of each interfacial architecture. The results given in Table II show that SiC acted as a strong interface (730MPa) relative to the other materials, but we were unable to demonstrate significant work of fracture for any of the laminated structures, possibly due to the fact that the interface layers were too thin (<1μm). It was expected that all second phase interface materials, especially the weak interfaces, would act to increase damage tolerance by mimicking the type of fracture pattern pictured in Figure 5, which shows the fracture surface of a scallop shell consisting of calcite laminates with weak protein interfaces that yielded a 30x increase in the work of fracture[13] compared to monolithic calcite. Figure 6, which shows the fracture surface of a $Si_3N_4$-$TiO_2/SiO_2$ specimen, indicates brittle fracture without significant delamination that would yield the type of textured fracture pattern consistent with a high work of fracture resulting from interfacial energy dissipation.

**Table II.** Strength of $Si_3N_4$ with Designed Interface

| Material | Average Flexural Strength (MPa) |
|---|---|
| SN-BN | 369 |
| SN-TiO2/SiO2 | 371 |
| SN-SiC | 730 |
| SN-SiO2 | 312 |

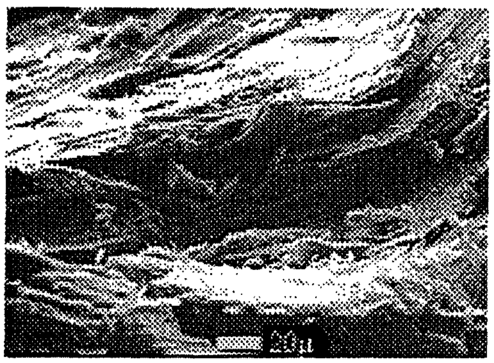


**Figure 5.** Scallop Shell Fracture Surface Indicating High Work of Fracture

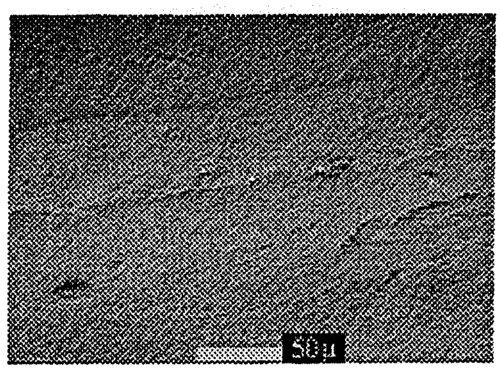


**Figure 6.** $Si_3N_4$-$TiO_2/SiO_2$ Fracture Surface

Microstructural Orientation

By incorporating β-$Si_3N_4$ seed crystals in the tape casting slip, $Si_3N_4$ microstructures were produced with elongated acicular grains oriented in the tape casting direction. Hiroa et al.[3] have demonstrated increased strength, toughness, and Weibull modulus via this process. In the current study, $Si_3N_4$ tapes with 2wt% β seed crystals (~3-5μm in length) and 7.25wt% $Al_2O_3$, 2.5wt% $Y_2O_3$ and 0.25wt% $ZrO_2$ as sintering aids were used to fabricate laminated specimens. Also, $Si_3N_4$ laminates containing no β seed crystals, as well as dry pressed $Si_3N_4$ specimens were fabricated for comparison. These materials were gas pressure sintered at

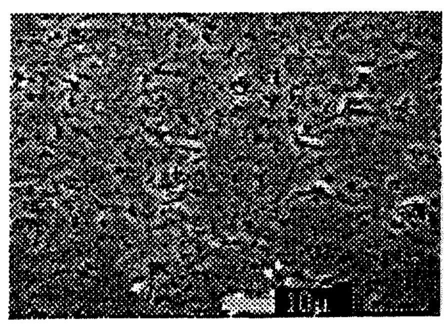


**Figure 7.** Oriented $Si_3N_4$ Microstructure

1810°C under a nitrogen gas pressure of 0.7MPa for three hours, followed by a further hour at 10MPa. Figure 7 shows a microstructural image of the top of a laminated specimen containing 2wt% β seed crystals. The casting direction in this photo was from left to right. The elongated β grains have grown during sintering to a length of ~10μm and it is apparent that acicular alignment has occurred in the casting direction.

Room temperature four-point flexural tests were conducted on eight specimens of each material, and chevron notch toughness measurements were conducted on five specimens for two of the laminated materials as indicated in Table III. The results in Table III indicate that laminated $Si_3N_4$ materials exhibit significantly higher strengths as compared to dry pressed $Si_3N_4$, due in part to the fact that the flaw size within the laminated structures is limited to the thickness of the individual tape layers. It appears that microstructural orientation in the casting direction leads to greater breaking consistency, as indicated by the reduction in flexural strength standard deviation. However, microstructural orientation did not yield a significant increase in the strength or toughness of the laminated $Si_3N_4$. Further microstructural development and greater acicular grain growth may be necessary in order to achieve higher strengths with toughnesses in excess of $10 MPam^{1/2}$ as described in the literature.[3] It is interesting to note that when the 2wt% β tapes were stacked such that the oriented acicular grains were aligned perpendicular to the length of the flexure specimen, a 200MPa reduction in strength was observed. This strength reduction confirms the anisotropic nature of the oriented microstructures.

**Table III.** Mechanical Property Results for Oriented Microstructure Study

| Material Architecture | Ave. Flexural Strength and St. Dev. (MPa) | $K_{IC}$ (MPam $^{1/2}$) |
|---|---|---|
| Dry Pressed $Si_3N_4$ | 715 (80) | --- |
| Laminated $Si_3N_4$ | 924 (101) | 5.76 |
| Laminated $Si_3N_4$ - 2% β | 920 (59) | 5.81 |
| Laminated $Si_3N_4$ - 2% β (β aligned perpendicular to specimen length) | 711 (92) | --- |

## *II. LOM Processing of $Si_3N_4$ Aerofoils*

LOM processing was performed to determine the compatibility of CCI's proprietary $Si_3N_4$ tape composition with the LOM fabrication process. Since the thermocompression stage used for manually laminated multilayer ceramics is not applicable for the LOM process, tape bonding experiments were conducted to determine an effective spray solution that would provide sufficient interlayer adhesion to allow for the fabrication of 3-dimensional $Si_3N_4$ components by LOM. Initial experiments evaluated ethyl alcohol, toluene, hexane, and isopropyl alcohol by spraying a thin layer of each onto a piece of $Si_3N_4$ tape, then laminating a second piece of tape and applying a 0.7MPa load for 10 seconds to mimic the load applied by the LOM roller. Although ethanol yielded the best results, there were pockets of non-bonded areas within the laminates which had occurred due to the rapid evaporation of the solvent prior to lamination. Further experiments demonstrated that the addition of either binder or plasticizer to the solvent spray would suppress the evaporation of the solvent and allow for more uniform bonding. Similar results have been reported previously.[12] Following the evaluation of various amounts of binder and/or plasticizer addition to the ethanol, a 10wt% polyvinyl butyral (PVB) in ethanol solution was selected for LOM processing because it demonstrated uniform bonding with relatively low organic content (10wt%).

LOM processing of $Si_3N_4$ components was performed using a LOM 2030 machine. The system is not configured for automated processing of green ceramic tapes and therefore it was necessary to manually laminate through the application of the bond solution followed by manually rolling each layer of tape prior to laser cutting. Three-dimensional aerofoils were fabricated using CCI's $Si_3N_4$ tapes and the 10wt% PVB in ethanol interlayer bond solution. The laser power was constant at 67% with a beam radius of 0.005" and speed of 10"/sec. Tile size of the cross-hatched excess tape was 0.25". The aerofoils were decubed, subjected to a binder burnout cycle and densified via the gas pressure sintering process described previously. The green-state aerofoils (prior to sintering) are pictured in Figure 8. During sintering, delaminations occurred, which indicates that although the bond solution provided sufficient interlaminar tape adhesion to complete the LOM process, it did not provide the intimate bonding that is necessary for strong interfaces and structural integrity in a dense component. This indicates that an additional processing stage, such as dry bag isopressing, should provide stronger interlaminar bonding during sintering. In order to remove all traces of the laminate architecture however, it may be necessary to introduce a warm bag isopressing process.

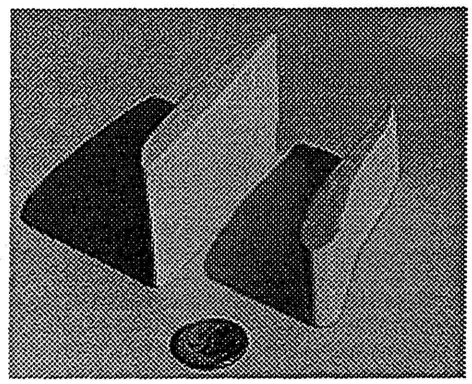

**Figure 8.** Green-state $Si_3N_4$ Aerofoils

## DISCUSSION AND CONCLUSIONS

This study on the lamination of $Si_3N_4$ ceramic tapes suitable for LOM fabrication investigated three different design approaches in an attempt to enhance the mechanical properties. While it has been found that the sintered properties of laminated $Si_3N_4$ are superior to those of non-laminated $Si_3N_4$ (924MPa versus 715MPa, respectively), this is only true if intimate interlaminate bonding has been achieved prior to sintering.

To facilitate the use of $Si_3N_4$ tapes in the LOM process it was necessary to "stick" the individual tape layers together so that they could be stacked and laser cut without curling. A number of adhesives in the form of solvent sprays were investigated and it was concluded that a 10wt% PVB in ethanol solution was the most effective for this purpose. Unfortunately, delamination occurred during the binder burn-out cycle, and without post processing (such as isopressing) of the LOM shape prior to binder burn-out and sintering it was not possible to obtain a sintered component with structural integrity and good mechanical properties.

Three approaches for enhancing the properties of manually laminated tapes were investigated in an effort to identify material designs which can be incorporated into the LOM fabrication process. The first approach involved the fabrication of a plate that was functionally graded from a 50wt% $Si_3N_4$/50wt% SiC interior to a 100% $Si_3N_4$ exterior. The resulting FGM exhibited an estimated surface compressive stress of 100MPa, which should improve the damage tolerance, thereby extending its performance in wear and structural applications. Compressive surface stresses have been investigated in the past[24] in order to improve the ballistic performance by extending the time to failure of the back surface of the ceramic armor tile. If there is a large impedance mismatch in the bi-material system (in this case, $Si_3N_4$ and SiC) then the armor will prematurely fail at the laminate interfaces rather than at the back surface of the tile. It is proposed that functionally grading the composition will minimize the impedance mismatch and thereby allow the back surface compressive stress to extend the time to failure. To date, these graded armor plates have not been ballistically tested.

The second approach involved the application of a second phase material between each of the laminates. The composition of this second phase can be designed to bond the layers together during LOM fabrication as well as to provide a strengthening and/or toughening mechanism in a sintered component. Of the four different laminate coatings investigated, $SiO_2$, $TiO_2/SiO_2$, and BN significantly reduced the strength to approximately 350MPa without improving the damage tolerance. The coating of SiC (which resulted from the in-situ reaction between $SiO_2$ and sugar) resulted in a strength of 730MPa but with very little increase in the work of fracture. No energy absorbing delamination was observed and only brittle fracture resulted. Electron microscopy revealed that these interfacial layers were <1μm and were discontinuous in nature. Further work is required to optimize the layer thickness in order to achieve enhanced damage tolerance.

The third approach involved the fabrication of specimens which contained an oriented microstructure obtained from the alignment of acicular $\beta$-$Si_3N_4$ grains during tape casting. Although laminated $Si_3N_4$ specimens with oriented microstructures did not exhibit improved strengths and toughnesses compared to non-oriented laminated $Si_3N_4$ (approximately 920MPa and $5.8MPam^{1/2}$), they showed considerably better reproducibility. When the flexural strength was evaluated perpendicular to the alignment of the acicular grains, the strength dropped to 711 MPa, thereby indicating the anisotropic nature of the aligned microstructure.

In summary, this work has shown that the nature of LOM fabrication can be used to create materials which possess designed architectures based on the merits of lamination. Laminated $Si_3N_4$ structures are superior in strength to dry pressed $Si_3N_4$, provided that intimate bonding is achieved between each of the layers. This evaluation confirmed the potential to fabricate functionally graded laminates with designed properties and it also demonstrated the ability to produce oriented $\beta$-$Si_3N_4$ microstructures with high strength and good reproducibility. The most versatile laminated architectural design approach may be interfacial design. The introduction of an interfacial second phase material (such as BN or SiC) within the bond solution used to stick the tapes during LOM processing should be explored further for the production of materials with designed fracture behavior.

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