1 of 2

Metals and Ceramics Division

DEVELOPMENT OF IMPROVED PROCESSING AND EVALUATION METHODS
FOR HIGH RELIABILITY STRUCTURAL CERAMICS FOR
ADVANCED HEAT ENGINE APPLICATIONS, PHASE I

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EXECUTIVE SUMMARY

This report documents the accomplishments of an extensive four year Processing for Reliability R&D program conducted at Saint-Gobain/Norton Industrial Ceramics Corporation's Northboro Research & Development Center and funded by the Department of Energy through Martin Marietta Energy Systems, Inc. The program goals were to develop and demonstrate significant improvements in processing methods, process controls and non-destructive evaluation (NDE) which can be commercially implemented to produce high reliability silicon nitride components for advanced heat engine applications at temperatures to 1370°C.

The program goals were addressed by focusing on a Si_3N_4 -4% Y_2O_3 high temperature ceramic composition and hot-isostatic-pressing (HIP'ing) as the method of densification. Quantitative mechanical property targets for tensile strength and stress rupture performance were established and were used as decision point criteria during the course of the program. The plan called for the development of colloidal methods to allow high quality near net shape forming of a reasonably broad range of green body geometries. The geometry chosen for demonstration was the variable diameter buttonhead tensile rod which served to define a suitably challenging forming requirement. The tensile rod is 165 mm long with 16 mm "buttonhead" end grip sections and a 35 mm central gage length with 6 mm diameter. Besides being a suitable forming geometry, through tensile testing, the tensile rod afforded a direct means to assess product quality relative to the strength and stress rupture targets. Furthermore, the resultant property database provides an invaluable resource for future engineering design efforts which utilize advanced silicon nitride material.

The program was conducted by performing a series of complete process cycles (iterations) - powder processing, forming, HIP'ing, machining - with each cycle producing about 75 tensile rods. Each iteration served as an experiment in a test matrix which was designed with the key process parameters as variables. After the period of process experimentation, the plan called for a demonstration of the optimum process involving production and testing of over 300 tensile rods. The goal was to have the mean room temperature tensile strength of specimens from this final set equal to 900 MPa with a variability equivalent to a Weibull distribution with threshold stress of 0 MPa and shape factor (modulus) of 20. The elevated temperature goals were a mean 1370°C tensile strength of 500 MPa and a 1230°C, 350 MPa tensile stress rupture life of 100 hours.

The program was conducted following six major tasks, Table I, each of which was pursued according to requirements and milestones specified within the contract statement of work. The program plan involved three successive stages of processing research. Stage I was conducted over the first two year period and had as major objectives : 1) comparing injection molding and colloidal consolidation process routes, and selecting one route for subsequent optimization , 2) comparing the performance of water milled and alcohol milled powder and selecting one on the basis of performance data, and 3) adapting several NDE methods to

the needs of ceramic processing. The NDE methods considered were microfocus x-ray radiography, computed tomography, ultrasonics, NMR imaging, NMR spectroscopy, fluorescent liquid dye penetrant and x-ray diffraction residual stress analysis.

Table I: Major Tasks in the Program

•	TASK 1:	Material Selection and Characterization
•	TASK 2:	Material Processing and Process Control
•	TASK 3:	Development and Application of NDE
•	TASK 4:	Property Testing and Microstructural Evaluation
•	TASK 5:	Reporting
•	TASK 6:	Quality Assurance

A requirement for conclusion of Stage I (1/31/91) was a comparison of databases generated in the Injection Molding (IM) and Colloidal Consolidation (CC) baseline iterations. On the basis of this comparison, it was required to select one of the two forming techniques for the remainder of the program, with the approval of the ORNL technical monitor.

Data obtained from the forming and testing of net shape formed (NSF) tensile rods and 50 mm diameter cylindrical (MLP) specimens were used in the comparison of the IM and CC processes. Specific data used in this comparison included: 1) yield at each major processing sub-step, 2) total process yield, 3) total process cycle time, 4) green density uniformity, 5) room temperature average tensile strength and Weibull modulus from tensile testing iteration NSF specimens, 6) high temperature average tensile strength from NSF specimens, 7) fracture toughness from MOR flexure bars machined from NSF specimens, 8) stress rupture data from MOR flexure bars machined from NSF specimens, and 9) formability of MLP specimens.

The data which favored IM relative to CC were the total process yield and the uniformity of green density. CC on the other hand was found to offer a considerably shorter total process cycle time, significantly greater averages for room and elevated temperature tensile strength and large section (MLP) formability in the sense of demonstrated capability to process specimens free of macroscopic drying/dewaxing cracks.

The overriding goal of the program was processing methodology capable of producing specimens with an average tensile strength of 900 MPa and high reliability, which is adaptable to large cross-sections, such as that of the MLP specimens. The CC forming technique had the advantage in both respects, on the basis of these iteration data. The baseline CC room temperature average tensile strength (692 MPa) was 52% higher than that of the IM route (454 MPa). Furthermore, several CC specimens had strengths in excess of the 900 MPa goal, with one being in excess of 1000 MPa. In comparison, the maximum strength recorded in the

IM iteration was 663 MPa. Formability was found to be a serious problem for larger cross-sections using the IM process. Optimal conditions of the dewax unit operation for MLP specimens were not achieved and cracking during dewaxing remains as a technical barrier in need of resolution for large cross-sections.

On the basis of demonstrated attainable strength and MLP formability, the colloidal consolidation process route was selected and approved as the forming technique for the remainder of the program. The issues of low yield and low Weibull modulus found in the baseline iteration were to be addressed at the beginning of the Stage II effort.

Eighteen process iterations were completed during Stage II over a 15 month period. Table II provides a strategical view of the effort relative to the three areas of emphasis: processing methods, process control and NDE. The outcome of the processing research was an environmentally sound, closed loop colloidal processing methodology. The process starts with aqueous vibration milling using Si_3N_4 milling media, followed by magnetic separation, filtration and dilution water removal. There is no need to dry the milled powder so uninterrupted colloidal processing from milling to casting is achieved, which translates into significant reduction in common types of contamination.

Table II: Process Optimization Strategy

The process control research employed experimental design methods to establish cause-effect relationships involving key process variables identified during Stage I. Control parameters were defined during the

course of this iterative experimentation and statistical process control (SPC) methods were implemented to assure process reproducibility. Notable examples of innovation include a method for control of the colloidal consolidation process (pressure casting operation) for formation of a uniform density green microstructure, HIP cycle definition which assures a high toughness acicular grain microstructure at greater than 99.5% theoretical density, and a machining methodology for the cylindrical tensile bars which maintained control of strength impairing surface damage.

NDE methods were customized during Stage II to provide novel characterization tools found necessary in the effort to establish cause-effect relationships. NDE played a crucial role as well in the areas of process monitoring and in-process flaw detection.

The advances in process technology realized during Stage II are reflected in statistics of flaw detection obtained by microfocus x-ray radiography (MFX). MFX data on average size and frequency of defects in HIP'ed tensile bars for the two baseline iterations and several Stage II iterations are plotted in Figure I. These data represent a grouping of results for pores, inclusions and agglomerates detected in the gage length volume. Clearly, dramatic improvements are suggested by these results.

Figure I: Flaw Statistics from MFX Evaluation of Iteration Samples

The material produced by the final Stage II optimized process has been given the designation NCX-5102 silicon nitride. According to plan, a large number of specimens were produced and tested during Stage III to establish a statistically robust room temperature tensile strength database for this material. Six process cycles were needed to produce the necessary set of approximately 400 tensile bars. These cycles followed the SOP established during Stage II. The fabrication and testing effort was accomplished during the seven month period May

through November, 1992.

The process demonstration provided experience and data which suggest that NCX-5102 truly ranks as a world class structural silicon nitride material. The test program established a mean tensile strength of 997 MPa for the set of 320 tensile rods which fractured within the one cubic centimeter uniformly stressed gage section. More than 80% of the samples had strengths above the target value of 900 MPa and approximately 50% had values in excess of 1 GPa, as is evident from the strength data histogram, Figure II.

The strength distribution for the sample set was determined by SEM fractographic analysis to be multimodal with several flaw populations contributing to the strength defining fast fractures. The range of the data was from a low value of 540 MPa to a peak value of 1237 MPa. A 2-parameter Weibull fit of the complete data set without the necessary competing risk analysis suggests a Weibull modulus of 10.4. However, competing risk data analysis suggests that the strength distribution associated with process related, intrinsic strength impairing flaws is best represented instead by a 3-parameter Weibull model, Figure III. Approximately one-half of the data fall into this category. The other half primarily involved machining damage related failure origins and define a distinctly different strength distribution.

Figure II: Histogram of 320 Stage III Tensile Strength Data

The intrinsic strength distribution has a threshold strength equal to 665 MPa which suggests that NCX-5102 is intrinsically more reliable

than the program target material envisioned to have a (2-parameter) Weibull modulus of 20.

Figure III: NCX-5102 Cumulative Probability of Failure for Intrinsic Tensile Strength Data from Competing Risk Analysis.

Highlights of the Stage III process demonstration and resultant database are included in the main text of the report, along with a synopsis of the NCX-5102 aqueous based colloidal process. The R&D accomplishments for Tasks 1-4 are discussed in detail in Appendices 1-4, while the tensile strength - fractography database for the Stage III NCX-5102 process demonstration is provided in tabular form in Appendix 5. These appendices serve to supplement the main text and provide a complete account of the Processing for Reliability program.

Thus, in summary, the following has been attained after this four year advanced processing R&D effort. A material (NCX-5102) having reliability significantly better than program goals and tensile strength at the 1 GPa level with fracture toughness approaching 7 MPa $\sqrt{m}$ has been developed using an innovative closed loop aqueous process operation. In addition, an unprecedented tensile strength database for the advanced ceramic material silicon nitride has been established and is available for engineering/design utilization. Finally, the validity of in-process use and relative power of all the currently available NDE methods has been shown for the efficient manufacture of high quality advanced ceramic materials.

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DEVELOPMENT OF IMPROVED PROCESSING AND EVALUATION
METHODS FOR HIGH RELIABILITY STRUCTURAL CERAMICS FOR
ADVANCED HEAT ENGINE APPLICATIONS, PHASE I

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ABSTRACT

This report documents the accomplishments of an extensive four year DoE funded Processing for Reliability R&D program conducted at Saint-Gobain/Norton Industrial Ceramic Corporation's Northboro Research and Development Center (NRDC). The research program had as goals the development and demonstration of significant improvements in processing methods, process controls and nondestructive evaluation directed towards the production of high reliability silicon nitride components for advanced heat engine application. A silicon nitride - 4 w/o yttria composition was used and densification was performed by glass encapsulation hot isostatic pressing (HIP'ing). The material developed in the program has been designated NCX-5102.

The program focused on near-net shape forming the buttonhead tensile bar geometry which allowed a direct means of monitoring product quality and establishing a comprehensive tensile strength database. Extensive NDE and fractography data were generated to establish the nature of failure precursors and their relationships with process parameters. The aqueous based colloidal consolidation process was optimized relative to stringent mechanical property targets. The process includes an innovative closed loop system of uninterrupted colloidal processing, from milling to shape forming, which effectively circumvents traditional sources of contamination. The process demonstration at the end of the program provided over three hundred samples and a corresponding mechanical properties database which suggests that NCX-5102 follows a three parameter Weibull strength distribution with a threshold tensile strength of 665 MPa and a mean tensile strength of over 1 GPa.

INTRODUCTION

This report discusses highlights of a silicon nitride processing methodology that has been developed in the course of a major four year DoE funded program in processing for reliability. The program focused on the attainment of high strength and reliability through the identification and subsequent control of strength degrading flaw populations. The material produced by the resultant process has been designated NCX-5102 and consists of a silicon nitride -4% yttria composition which is densified by use of glass encapsulation HIP'ing.

An account is provided of developmental efforts which have resulted in a colloidal processing methodology for the production of high strength, high reliability silicon nitride components for advanced heat engine application at temperatures to 1370°C. The effort has concentrated on the near net shape fabrication of large aspect ratio, axisymmetric buttonhead tensile bars. This geometry served as a challenging forming requirement, sufficient for development of a general shape forming capability and it also provided a direct means to assess tensile strength levels attributable to the process.

The program was conducted in three stages, namely: 1) baseline process definition, 2) process optimization and 3) large scale production demonstration. In Stage I, two distinct processing routes - injection molding and colloidal consolidation (CC) - were evaluated and the CC route was found to offer the best potential for quality and cost-effective manufacturing. In Stage II, the CC process was optimized relative to stringent mechanical property targets. The overall program goal was to achieve a mean room temperature tensile strength of 900 MPa with a (2-parameter) Weibull modulus of 20, a mean 1370°C tensile strength of 500 MPa and a mean 1230°C, 350 MPa tensile stress rupture life of 100 hours.

A "closed loop" aqueous based powder beneficiation - colloidal consolidation methodology was the basis of the green ceramic production strategy. Large scale batches (30 kg) of silicon nitride - 4% yttria powder were milled in water and the resulting slurry was used to cast as many as 200 tensile rods. The powder which is derived from a diimide process was used as starting silicon nitride powder. The processing was conducted within a class 10000 clean room. More than thirty full scale batches were processed which allowed the development of SPC charts for several chemical and physical properties of the powder and slurry for monitoring of variations in raw material as well as the milling, filtration and concentration operations. To ensure process repeatability, a comprehensive standard operating procedure (SOP) was established for each subtask of each unit operation.

The casting operation was optimized using a custom designed multi-station casting rig. The apparatus was computer controlled according to a pressure profile established to maintain a uniform casting rate. This results in a well controlled green microstructure having minimal density variation.

The process optimization strategy involved a series of process iterations. The tensile specimens produced in each iteration were tested to determine the tensile strength distribution representative of

the iteration. Each iteration served as an experiment in a test matrix which was designed with the critical process parameters as variables. Extensive NDE and fractography data were generated to establish the nature of failure precursors for guidance on the process improvements necessary for strength and reliability enhancement in subsequent iterations. The resulting data for the set of experiments were used to define the optimum, total process, control variable levels.

The process control research employed experimental design methods to establish cause-effect relationships involving key process variables identified during Stage I. Control parameters were defined during the course of this iterative experimentation and statistical process control (SPC) methods were implemented to assure process reproducibility. Notable examples of innovation include a method for control of the colloidal consolidation process (pressure casting operation) for formation of a uniform density green microstructure, HIP cycle definition which assures a high toughness acicular grain microstructure at greater than 99.5% theoretical density, and a machining methodology for the cylindrical tensile bars which maintained control of strength impairing surface damage.

Several NDE techniques were employed, including microfocus radiography (MFX), ultrasonics (UT), computer tomography (CT), fluorescent liquid dye penetrant (LDP) and nuclear magnetic resonance (NMR). The techniques were adapted for application to various steps of the process. The detection capabilities of each technique were determined quantitatively with appropriate reference standards which were prepared at Northboro R&D Center. The NDE methods were customized during Stage II to provide novel characterization tools found necessary in the effort to establish cause-effect relationships. NDE played a crucial role as well in the areas of process monitoring and in-process flaw detection.

The cylindrical buttonhead tensile specimens were machined to the ORNL design with a gage diameter of 6.0 ± 0.1 mm. All specimens for the main body of strength data were machined using a specially designed SOP developed for this geometry. Two comprehensive studies were pursued to establish optimum machining practice. The first involved a machine shop qualification which established specifications for control of buttonhead failures. The second involved specifications for control of machining damage in the gage length which influences tensile strength of NSF bars.

Optical fractography and scanning electron microscopy were performed on all specimens. Low and high magnification micrographs were taken of each fracture surface and flaw origin. Energy dispersant spectroscopy was performed at each origin to determine if any impurities were present. The location, type and size of each flaw were noted, measured and tabulated for database evaluation.

The Stage III demonstration provided over three hundred samples and a corresponding mechanical properties database. Fabricability of large cross section components was assessed by forming 50 mm diameter samples. Mechanical properties of these samples were established by testing specimens machined from locations across the samples.

COLLOIDAL CONSOLIDATION PROCESS

POWDER PROCESSING

The aqueous closed loop process is compared with the conventional alcohol milling approach in Figure 1. Various physical and chemical characterization techniques were employed both for the raw material and the milled powder. Although x-ray diffraction of the starting Ube powder found very little variation in α -phase from lot to lot, measurable variations in surface area (shown in Figure 2), particle size and oxygen content were found. In most cases, milling conditions were adjusted to bring the powder properties within the specified control limits. However, the fifth lot of powder, "Lot E", in spite of meeting all physical property specifications, showed very different colloidal casting behavior. Further surface chemical examinations (courtesy Dr. S. Malghan, NIST) suggested significant shift in the iso-electric point (IEP) for the Lot E powder (as compared to Lot D) as shown in Figure 3. Other lots of powder showed similar behavior to that of Lot D. Various surface treatments have been developed to control the IEP and hence the casting behavior. IEP was also included as a process control parameter.

ALCOHOL ROUTE

Alcohol Milling
↓
Mag Separation
↓
Dry
↓
-325 Mesh Screening
↓
Disperse In Water
↓
Mix

AQUEOUS ROUTE

Aqueous Milling
↓
Mag Separation
↓
Filtration (5 μ m)
↓
Concentrate

Mix → Pressure Cast ← Concentrate
↓
Cast Body

Figure 1: Comparison of Aqueous and Alcohol Based Powder Processing Methods

Figure 2: Surface Area for Various Grades and Lots of UBE Silicon Nitride Powder

Figure 3: Zeta Potential vs. pH for Si₃N₄ Lots D and E

SLURRY DEVELOPMENT AND CHARACTERIZATION

A comprehensive slurry characterization methodology was developed using viscosity, pH, and centrifuge packing density measurements in combination with the NMR (Nuclear Magnetic Resonance) spin-lattice parameter (T_1). Slurry characterization was further refined to predict casting behavior. A "Casting Rate Slope" parameter was defined and developed as a process control measure. The procedure is briefly described as follows: a fixed amount of slurry is cast at a constant pressure on an established porous material. Cast thickness is monitored at fixed time intervals. Thickness squared is plotted as a function of casting time and the slope of the line is defined as the "Casting Rate Slope" (CRS). An Upper Control Limit (UCL) for CRS is defined as shown in Figure 4. Slurries having CRS values above UCL are rejected, as high CRS correlates with unacceptable density gradient levels in the cast body as described in the next section.

Figure 4: Slope of Casting Rate Curves for Various Lots of Powder

CASTING OF NET SHAPE FORMED (NSF) TENSILE BARS

The casting of concentrated ceramic suspensions is influenced by the mold design and the slurry properties, especially the CRS as described in the previous section.

The effect of mold design on the cast density variation has been addressed by Pujari et al¹ previously. The effect of total mold filtration surface area was analyzed using Computed Tomography (CT). From that analysis, an optimum mold design was established for subsequent use.

Various slurry batches for which CRS was defined previously were utilized to cast tensile bars using the optimized mold. The effect of slurry CRS is illustrated in Figure 5 by the bent shape of a HIP'ed tensile rod. This rod was cast from a slurry which had a CRS value above UCL. Bending during the HIP process results from the radial green density gradient shown by the ultrasonics C-scan in Figure 6. The correlation of CRS with the cast density gradient established in this program apparently has not been previously recognized, considering the lack of discussion of the concept in the literature. The correlation follows from the fact that excessive casting rates provide inadequate time for the optimum packing of powder particulates during filtration.

All test bars for testing and reliability demonstration were fabricated from slurry batches showing CRS below UCL level. The process yield at the casting unit operation was computed to be upwards of 90%.

Figure 5: Density Gradient Effect on Part Tolerance

Figure 6: UT Image of Green Tensile Bar Showing Density Gradient

HOT ISOSTATIC PRESSING

The net shape formed (NSF) bars were hot isostatically pressed (HIP'ed) using ASEA glass encapsulation technology. The HIP process was optimized using pressure, time and temperature parameters to assure full densification and development of an elongated microstructure (Figure 7) for desired fracture toughness (K_{Ic}). Control limits for density and fracture toughness were defined as $>99.5\%$ TD and $5.8 < K_{Ic} < 6.2$ MPa $\sqrt{m}$, respectively. It was imperative to reproduce K_{Ic} within specified control limits in order to examine the process improvement due to the flaw reduction, a key objective of this program. It was, however, found that the HIP process contributed to the process variability by nature of its being a batch process. Better understanding of the thermal profiles during the HIP cycle and/or incorporation of a continuous sintering cycle will further enhance the reliability of this improved process. A limited effort has been launched towards understanding the temperature gradients during sintering in general and in the HIP cycle in particular.

Figure 7: SEM Micrograph Showing High Toughness Elongated Microstructure

MACHINING PROCESS OPTIMIZATION

Four machining procedures were evaluated for their influence on tensile strength. A total of 72 tensile specimens from 3 HIP runs were machined and tested. Consistent with the focus on machining damage effects, the specimens were not given heat treatments for the purpose of this study. To properly evaluate the procedures, only those specimens that failed from surface flaws within the gage length were considered (64 of 72).

Customary practice expresses surface finish specification in terms of the average roughness R_a . Early Stage II work established the need to revise the R_a specification from 16 μin (0.4 μm) to 10 μin at the buttonhead radius and to 8 μin along the gage length. The current study maintained these R_a specifications but considered different rough grinding procedures including intermediate grinding steps, diamond wheel type and depths of cut. On the basis of the grinding parameters employed, the machining procedures would be ranked according to operational precision from #1 to #4, with #4 being the most precise.

In spite of the major differences in operational precision, the resultant tensile strength data showed no statistically significant dependence on procedure, Figure 8, even though R_y (maximum peak to valley) Talysurf surface finish values were significantly higher for procedures #1 and #2 when compared to procedures, #3 and #4, Figure 9.

The mean strengths found in this study were consistent with the 900 MPa room temperature target, given the absence of strength enhancing heat treatment. Therefore the primary consideration in choosing a machining procedure for Stage III was attaining a minimum variability of strength and high Weibull modulus. Since procedure #1 had the least variability, it was chosen as SOP for Stage III demonstration.

Figure 8: Mean Tensile Strengths Using Machining Procedures 1,2,3,4

Figure 9: Effect of Machining Procedure on the Surface Finish

TENSILE STRENGTH DATABASE

Over the course of the four year program, hundreds of tensile rods were fabricated and tested. The final Stage III demonstration involved over 300 samples which were tested to establish the room temperature fast fracture tensile strength distribution characteristic of the optimized process. In addition, more than 25 elevated temperature fast fracture (1370°C) and stress rupture (1230°C) tensile tests were completed as discussed below.

ROOM TEMPERATURE TENSILE TEST DATA

The tensile test database from the Stage III demonstration set includes fractography results on location, type and size of the failure origins obtained using optical and scanning electron microscopy. The majority of the room temperature specimens had failure origins at the surface within the uniformly stressed 6 mm diameter gage length. Two types of surface failure origins were identified; namely, machining flaws and amorphous areas that developed during the post-machining treatment step. Also, two distinct types of volume flaws were observed. One was a microstructural flaw characterized by a zone of microporosity. The other involved inclusions from contamination subsequently traced to a piece of processing equipment. The fractography results are summarized in Table 1 according to failure origin type. A typical machining flaw which includes a grinding groove and associated radial cracks as depicted by the liquid dye penetrant technique is shown in Figure 10. Fractography examples of the four flaw types are shown in Figures 11-14.

Figure 10: Liquid Dye Penetrant Fluorescence Microscopy (750X) Revealing 6 μ m Wide Grinding Groove and Associated Damage

Figure 11: Intrinsic Volume Failure Origin, 25°C 982 MPa Tensile Strength

Figure 12: Amorphous Surface Failure Origin, 25°C 985 MPa Tensile Strength

Figure 13: Inclusion Volume Failure Origin, 25°C 606 MPa Tensile Strength

Figure 14: Machining Fracture Origin, 25°C 1234 MPa Tensile Strength

Table 1: Stage III Fractography (25°C) Summary

Category	Type	Location	#
Intrinsic	Microporous	Volume	55
	Amorphous	Surface	107
	Unknown		8
Extrinsic	Inclusion	Volume	16
	Machining	Surface	134

In the statistical analysis discussed below, the surface amorphous flaws and the volume microstructural flaws were considered to comprise a set of intrinsic flaws, since they randomly occur within the standard processing cycle. On the other hand, the machining damage and inclusion flaws were classified as being extrinsic flaws, since they are subject to control by means unrelated to the silicon nitride process per se.

The database includes a total of 320 valid tensile tests. There were an additional 35 specimens which failed in the non-uniformly stressed regions of the specimen which have been excluded from this summary. The 320 strength data are presented in a cumulative probability of failure plot using standard Weibull coordinates in Figure 15. The data range from 540 to 1237 MPa and have a mean value of 997 MPa. The strength and fractography data are tabulated in Appendix 5. The nonlinear character of the distribution with multiple inflections suggests that a 2-parameter Weibull fit of this data ($\sigma_0=1038$ MPa, $m=10.4$) would be inappropriate and that the multimodal nature of the data should be represented using competing risk analysis.

Figure 15: Cumulative Probability of Failure Plot of Stage III Tensile Strength Data

The multimodal analysis was pursued by considering the group of 320 strength data as being composed of two sets, with one set ($n=170$) representing strengths of the intrinsic defects and the other ($n=150$) representing strengths of the extrinsic defects, Figure 16. Competing risk analysis reveals that the extrinsic strength data dominate the nonlinear low strength tail of the overall distribution. The plot of their distribution is similar to that of Figure 15. The intrinsic strength data on the other hand has a distinctly different character which is well represented by a 3-parameter Weibull model with a threshold stress of 665 MPa, a scale value of 444 MPa and a shape value of 3.92. The intrinsic strength data are plotted in Figure 17 along with this 3-parameter model and also with a 2-parameter fit which clearly is a poor representation of the data. The line to the left of the data represents the program target material having a mean tensile strength of 900 MPa and a 2-parameter Weibull modulus of 20.

Figure 16: Competing Risk Weibull Plot: Intrinsic vs. Extrinsic Failure Origins

From a reliability perspective, the important feature of the 3 parameter Weibull distribution is the existence of a threshold stress below which there is zero probability of failure². Physically this corresponds to a processing methodology which has succeeded in truncating the upper tails of the critical flaw size distributions. A threshold at the level indicated clearly has direct impact on design systems used in fielding reliable ceramic components. For instance, NCX-5102 with the 3 parameter distribution of Figure 17 would provide higher reliability at all stress levels when compared to the program target material, as indicated in Table 2.

Table 2: Probability of Survival at Given Stresses (MPa)

	Target	Weibull 2 Parameter	Weibull 3 Parameter
R99	735	766	802
R999	655	639	741
R9999	583	533	707
R99999	520	444	689
R999999	463	370	678

Figure 17: Cumulative Probability of Failure Plot of Intrinsic Strength Data

ELEVATED TEMPERATURE TENSILE TEST DATA

The potential of reaching the program's elevated temperature mechanical property targets was demonstrated during Stage II using a specialized SOP. Fast fracture strengths at 1370°C were found to range from 425 to 520 MPa with a mean of 477 MPa in 5 tests. Stress rupture lives at 1230°C equaled or exceeded 100 hours at 250, 300 and 350 MPa in separate tests, although not all tests at 350 MPa survived 100 hours.

It was found that processing conditions for optimum room temperature properties differed from the above SOP. The primary focus in the program was to establish strength and reliability improvements through flaw control using room temperature strength data as the measure of improvement. On this basis, the Stage III optimization focused on

SOP which favored room temperature characterization of NCX-5102.

Fifteen Stage III samples were tested to fast fracture at 1370°C. The mean strength was 396 MPa, with a range 344-452 MPa. There were 6 volume and 9 surface failures and fractographic examples of each are given in Figures 18 and 19.

Ten Stage III stress rupture tests were conducted at 1230°C. The target 100 hour lifetime was achieved at 250 MPa, but not at higher stress levels. The data from the Stage II and Stage III tests are shown in Figure 20 in a plot of applied stress vs. failure time.

Numerous processing steps were optimized to produce superior room temperature properties to demonstrate that flaw control can result in significant advances in the quality of silicon nitride. Additional processing optimization can be expected to provide improved high temperature properties beyond what has been accomplished in this program as was demonstrated by the investigation using the specialized SOP cited above.

Figure 18: Intrinsic Volume Failure Origin, 1370°C 405 MPa Tensile Strength

Figure 19: Machining Failure Origin, 1370°C 403 MPa Tensile Strength

Figure 20: Tensile Stress Rupture Data at 1230°C in Air for Stage II and Stage III Specimens

LARGE CROSS SECTION SPECIMEN STRENGTH DATA

The general applicability of the optimized process beyond NSF tensile rods was demonstrated by fabricating and testing 50 mm diameter, 150 mm long specimens. These have been referred to as MLP (machined from large piece) specimens, in that the specimens were machined into many flexure bars (3 x 4 x 50 mm) for assessment of the properties across the 50 mm section. Excellent fast fracture strength results were obtained both at room and elevated temperatures. As was found for the intrinsic tensile strength data discussed above, the flexure data are well represented by 3 parameter Weibull models, Figure 21. Threshold flexure strength values of 653 MPa and 517 MPa are predicted by these models for room temperature and 1370°C, respectively. The mean flexure strengths were 972 MPa (n=30) and 561 MPa (n=33), respectively.

Figure 21: Flexure Strength Data from Large Cross Section (MLP) Specimen

CONCLUSIONS

Using an iterative processing approach, each unit operation of the colloidal consolidation process and the process as a whole has been optimized. Closed loop aqueous processing incorporating powder comminution, slurry concentration and casting has been the key to the successful completion of the program with desired reliability capability. Equally significant has been the implementation of various powerful NDE techniques both for in-process control and for the identification of critical strength limiting defects. Use of NMR spectroscopy for slurry aging behavior characterization³, computed tomography (CT) for density gradient evaluation leading to optimum mold design,³ ultrasonic (UT) technique for in-situ monitoring of the casting process and density gradient evaluation in cast NSF bars⁴, microfocus radiography for volume flaw detection both in green and dense specimens and lastly liquid dye penetrant (LDP) approach for the detection of machining related damage are a few salient examples.

A comprehensive database has been generated through fabrication, testing and post mortem fractography of a large set (>300) of net shape formed tensile bars. Analysis of the data suggests a significant reduction in both flaw size and the frequency of flaw occurrence. Microfocus radiography data suggests a five fold reduction in flaw size (from 250 μm to 50 μm) and frequency of flaws (2.5/bar to less than 0.5/bar). This data agrees very well with the 100% increase in average tensile strength realized in the program.

Statistical analysis suggests that the truncation of large failure precursors affected by the processing strategy results in a three parameter Weibull strength distribution with threshold stress near 665 MPa. It follows that NCX-5102 is both stronger and more reliable than the targeted material characterized by a mean tensile strength of 900 MPa and 2 parameter Weibull shape factor (modulus) of 20.

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APPENDIX 1: MATERIAL SELECTION AND CHARACTERIZATION

MATERIAL SELECTION

A silicon nitride composition (with 4% yttria) was selected to perform the specified tasks and meet the required property goals. Ube silicon nitride powder was chosen for its purity because it was observed that many of the carbothermally produced powders (Kemanord and Stark) contain significant amounts of iron impurities which lower the strength of the densified materials as flaws. Ube Chemical was used as the source of silicon nitride throughout the program. This powder is a chemically derived product made by a thermal decomposition of silicon imide. The process begins with low temperature reaction semiconductor grade silicon tetrachloride with liquid ammonia to form silicon imide, followed by a first calcination step to form amorphous silicon nitride and second calcination step to form crystalline silicon nitride. The conditions used for the second calcination determine the particle size, surface area and morphology of the powder.

Three grades of Ube silicon nitride were used: Ube SN-E03, Ube SN-E05, and Ube SN-E10. The blend ratio was adjusted to control packing density. The high purity raw materials resulted in a high purity powder. Low iron levels have been found necessary to obtain optimum high temperature properties. The alpha silicon nitride content of this powder is typically >98% and there is no measurable free silicon. Although residual chlorine can be detrimental to high temperature properties, our process has ensured a Cl level <50 ppm. Residual carbon can be high for the Ube product and is monitored, but no direct effect on final properties was determined.

Molycorp was the source of the yttrium oxide powder used in the co-milled process and the yttrium nitrate powder used in the precipitation process.

The above composition milled in alcohol showed potential for meeting the targeted room and high temperature properties. In this program alcohol milled powder was chosen to develop the baseline capability employing the injection molding process. Subsequently, the 4% yttria silicon nitride composition with process improvement was processed in an aqueous medium. Deionized water with a resistivity ~ 18 megohm-cm passed through a 0.2 micron filter was used throughout the program.

MATERIAL CHARACTERIZATION

Silicon nitride stock powders were analyzed for chemical composition, impurities, and particle size distributions. Phase analyses were carried out by x-ray diffraction. Impurities were assessed by emission spectrographic analysis. The cationic impurities were determined by digestion of the powder and analysis by AA and ICP. The anionic impurities were determined by ion chromatography. Surface area and particle size distributions were determined by BET, sedigraph, and light scattering techniques to cover the range of fine particles. Analyses were carried out at each unit operation, and the tests required

at each step, as well as the operational ranges were defined within the process SOP. Besides chemical analysis of powders, impurities and additives, a broad range of physical analyses were specified, e.g. particle size distribution, surface area, morphology, phases.

Oxygen Analysis

Oxygen content in the silicon nitride powder was analyzed by the LECO method. The oxygen in samples combines with carbon at high temperature to produce CO which is analyzed by infrared detection. In the process which involved co-milling of Si_3N_4 and Y_2O_3 the detection of oxygen in the starting and in the milled powder was analyzed with fair certainty because the moisture content in the powder is small. Most of the oxygen in Si_3N_4 is in the form of silicon oxide or dioxide. Also, the moisture/water content on such powders is determined by Karl Fisher method and is always below 0.1%.

In the process which involved addition of the sintering aid by the precipitation technique, oxygen in the powder after yttria precipitation on the surface is a combination of oxygen generated during milling, the original oxygen in the powder, moisture content of the powder and the colloiddally precipitated Y_2O_3 . Therefore, two values of the oxygen are determined: 1) from the powder after controlled drying, which contains the contributions from all the sources discussed above and 2) after calcining the powder at high temperature in N_2 .

Yttria and Oxygen Values

Due to the calcination used to produce yttrium nitrate, varying levels of residual carbon may be encountered and are monitored. Thermal gravimetric analysis of yttrium salt showed that the material has $6\text{H}_2\text{O}$ molecules as specified. It decomposes to Y_2O_3 at $\sim 700^\circ\text{C}$ with a 70% weight loss. The formula used to specify the amount of yttrium salt needed to give 4w% Y_2O_3 has been modified. Instead of a factor of 3.5, a factor of 3.4 was used. Also, the TGA for $\text{Y}(\text{OH})_3$ showed that the full conversion to Y_2O_3 occurs between 800°C and 900°C with a 35% weight loss. Therefore the calcination of $\text{Y}(\text{OH})_3$ to 1000°C is needed to give a corresponding oxygen for Y_2O_3 . However, the oxidation of Si_3N_4 needs to be minimized. Various calcination treatments in vacuum and/or nitrogen to 800°C have consistently shown 0.5 w/o additional oxygen pick up.

The final value of the oxygen on the presintered bar as well as on the MOR bars after HIPing and machining has also been determined. For these determinations, the bar is crushed to small pieces, taking precautions that no contamination or oxidation occurs in the bar while crushing. These pieces (50-60 mg) are used for LECO analysis.

Analysis of Metallic Species

The metallic species were extracted by acid digestion of the powder. The powder was digested first in sodium hydroxide. The fused material was then dissolved in hydrochloric acid. The yttrium analysis was performed on this solution by atomic absorption (AA) technique. The dissolved solution was also analyzed by inductively coupled plasma (ICP)

technique. The choice of the equipment depends on the sensitivity of the determination of the element. For yttrium both AA and ICP were used; however, ICP gave a better sensitivity for the yttrium species. We have also determined yttrium by x-ray fluorescence (XFS). Emission spectroscopy technique has been used to analyze metallic impurities in the powder. This technique was used exclusively for aluminum, zirconium and iron, although the analysis is applicable to B, Ni, Cu, V, Na, Cr, Ca, Ti, Mg, and Li as well. The anionic species in the powder was analyzed by ion chromatography. The material was digested and the solution analyzed for anionic species.

Particle Size and Surface Area of the Powder

Both the surface area and the particle size distribution of the powders have been routinely measured to assess the extent of milling of Si_3N_4 powders, while simultaneously measuring the oxygen content. The particle size distribution has been determined routinely by two techniques: 1) sedigraph and 2) microtrac. These two instruments combined give a reasonable picture of the size distribution of the particles. We measure d_{10} , d_{50} , and d_{100} for a general comparison from batch to batch. The surface area is determined by multiple point BET gas adsorption using N_2 as the gas. These two combined measurements give a reasonable state of the milled powder along with the oxygen values.

There was enough lot-to-lot variability in the Ube powder to necessitate significant adjustment of milling conditions to achieve a consistent milled particle size distribution. Figure 1-1 shows the as received and milled average d_{50} particle size for Lots B, C and D. Within a lot there was no significant variation. Figures 1-2 and 1-3 show the result of a harpoon analysis for the drums of Ube silicon nitride powder of a single lot. This analysis indicates that although the differences in the variables of interest were significant when examining various drums within a lot, the differences within a drum were insignificant.

Rheological Measurements

Rheological measurements on the slurry have been performed by Bohlin rheometer model VOR and constant stress rheometer C.S. These two units together provide capabilities to analyze slurries completely in viscometry, oscillatory and relaxation tests. Constant stress rheometer also gave accurate values for the yield stress often used to interpret rheological data and their implications. The Injection molding compound was fully characterized rheologically using the capillary rheometer.

IEP Measurements

Another colloidal property monitored on incoming Ube powders was IEP done by Pen Kem 7000 acoustophoretic technique which not only determines the charge on the particles but also assesses the role of impurities and their extent on the powder surface. Lot E showed a significant difference in IEP from lots A through D (see Appendix 2). Various treatments were attempted to effect a change in the IEP with

varying degrees of success on a laboratory scale. Further scaleup optimization of these treatments is required. Prior to receipt of Lot F powder, several preshipment samples of various Ube lots were analyzed for isoelectric point and particle size distribution. The lowest isoelectric point Ube lots were selected for Lot F shipment.

Figure 1-1: D₅₀ Particle Size for As-received and Milled Powder Batches

Milling media

Submicron debris was a component of the final milled powder due to attrition during milling. The attrition rate varied slightly depending on conditions, but ranged from 0.2 to 1.0 w/o of the final milled powder. The media is basically the same composition as the powder, but since it has been densified by HIP'ing, it consists of beta silicon nitride. This submicron beta silicon nitride may have an influence on seeding for grain growth during HIP densification of the product.

CHARACTERIZATION OF THE MILLED SILICON NITRIDE SLURRIES

The water milled silicon nitride slurry, in the presence of the surfactant, has a pH of 9.0 + .1 and the isoelectric point of the powder is 5.5 + .1. Therefore, the milled slurry is a well deflocculated stable suspension, ideal for filtration. After filtration the entrapped material in the filter and the filtered slurry powders were analyzed for particle size distribution by SEM and Sedigraph and by BET measurements for surface area.

These measurements confirm that the slurry is indeed very well deflocculated. The SEM and sedigraph data show that d₁₀, d₅₀, d₉₀ for the particles do not change significantly by these filtrations. Also, more

than 93% of the slurry is recovered by this filtration.

Figure 1-2: Oxygen Level in As-received E03, E05, E10 Ube Powder

Surface impurities of the milled powders were characterized by x-ray photoelectron spectroscopy. The starting powder and the powder after milling with different amount of the surfactants were examined for surface impurities. The XPS data show less than two atomic percent aluminum and no detectable Zr impurities in the starting as well as milled powders. However, ICP and emission spectrographic analysis show different levels of aluminum and Zr in the milled powder. The values of Al and Zr in the powder by emission spectrographic analysis are

significantly higher than those of ICP values. The reason for this discrepancy has not yet been identified.

Figure 1-3: Surface Area of As-received E03, E05, E10 Ube Powder

CHARACTERIZATION OF INJECTION MOLDING BINDER

Thermal analysis was regularly used for the analysis of binders and plasticizers. More specifically, injection molding binders were measured for thermal conductivity, specific heat (DSC), glass transition temperature (DSC), and pressure-volume-temperature (p-v-t) correlation. Differential Scanning Calorimetry (DSC) and Gel Permeation Chromatography (GPC) techniques were used to characterize the virgin binder and the molding compounds. Melting peaks and the heat of transition for the virgin binder and the molding compounds were established for repeated heating cycles. These data were used to monitor and control the binder characteristics at various stages of the processing. These properties have also been used for the finite element analysis of the injection molding process. DSC and Gel Permeation Chromatography techniques were also utilized to characterize the virgin binder and the molding compound for QC purposes. Due to the experimental difficulties (caused by powder loading) GPC could not be performed on the molding compounds.

CHARACTERIZATION OF CASTING PLASTER MOLDS

Plaster molds used in the pressure casting process were characterized both chemically and physically. Chemical analysis determined metallic impurity levels by emission spectroscopy. Physical characterization consisted of mercury porosimetry measurements.

APPENDIX 2: MATERIAL PROCESSING AND PROCESS CONTROL

POWDER PROCESSING

All process equipment were set up inside a Class 10,000 hard-wall clean room, specifically constructed for this program. The room was divided into a vestibule (for dressing into clean room garments and monitoring of conditions such as temperature, humidity and pressure), a powder storage room and the main processing room. Pressure was maintained highest in the main processing room. A vibratory mill was set up for both semicontinuous operation (14 to 60 kg) and batch operation (4-11kg). High purity silicon nitride milling media were specially fabricated for this program. The media were shaped as cylindrical bodies with hemispherical ends. Vibration milling was used as compared to ball milling because it provides for continuous monitoring and sampling throughout the milling cycle. Lower solids contents can be milled without the excessive media wear associated with the higher impact forces of ball or attrition milling.

Except for the initial process iteration, water milling was used instead of conventional alcohol milling. Water milling had in the past been thought to promote hydrolysis and formation of surface oxide layers so that alcohol was the preferred medium for milling. The powders milled in alcohol contain at most a trace or no hard agglomerates at all and the soft agglomerates break up easily. In the presence of alcohol, the decomposition and/or hydrolysis of silicon nitride should not proceed actively. Silicon nitride powders milled in water are known to contain higher levels of hard agglomerates and oxygen for two primary reasons: post-milling processing steps (oven drying) and decomposition/hydrolysis of silicon nitride in the presence of water. We have been able to successfully mill silicon nitride powder in water by controlling the chemistry of the aqueous phase using surfactants. Aqueous milling grants a number of benefits such as lower cost, environmental compatibility and process flexibility. Given a post-milling concentration step, a very low solids content can be used which allows for filtration at smaller sizes and more efficient magnetic separation.

The primary function of filtration of the slurry was to remove agglomerates and any foreign objects than may have been introduced during milling and handling of the powder. If a slurry containing primarily minus 1 micron particles is filtered, then filtration at 10, 20, 30 micron should not present any problems. However, as the filtration size is decreased to 10 microns and finer, increasing resistance to filtration is observed due to increasing number of near-size particles. Therefore, a requirement for filtration to succeed is a well dispersed slurry. In this program, filtration sizes ranging from 2 to 80 microns were evaluated. The use of water as the medium allowed for dilution of the slurry so that filter sizes less than 10 microns could be successfully used. Magnetic separation of the milled slurry was performed using a high gradient magnetic separator. The slurry was recirculated through the separator for a fixed period of time.

After the low solids content slurry was filtered, a concentration step was used to dewater the slurry to achieve a high solids loading

that could be directly cast. Solids loadings of 65 to 74 w/o were easily achieved. Loadings above 74% were limited due to dilatency. Process equipment such as pumps can impart a higher shear rate than normally measured using a Brookfield viscometer, resulting in dilatency. Another advantage of this dewatering process was to decrease the level of residual Cl and F that could exist on the as-received Ube silicon nitride powder. Chlorine has been shown to be detrimental to high temperature properties.

W-Series Process

Initially, the sintering aid (yttria) was added by a precipitation of salt process, Figure 2-1. After aqueous milling and filtration the slurry was pumped in a closed loop to a precipitation tank. A yttrium salt was then added and the pH adjusted in a controlled manner to provide for precipitation of the hydroxide on the surface of the powder. The soluble product salt was then rinsed from the slurry to a level less than 50 ppm. The precipitated slurry was flocculated at this stage. A dispersant was added and the slurry concentrated to a level appropriate for casting, typically 72-74 w/o. The surface of the powder resulted in dispersion behavior similar to yttrium hydroxide. This approach had several advantages and disadvantages. The resulting slurry was extremely stable. Because the yttria was present as a hydroxide, there was no aging problem such as encountered with a co-milled route. Also, the surface hydroxide resulted in a partially flocculated slurry, and therefore easily redispersed after settling occurred during storage. Slurry produced by this method has been found to have a shelf life of months. In contrast, the co-milled product must be used within days and must be agitated continuously during that period. Due to the hydroxide, there would typically be a higher oxygen content (~0.5% higher) of the product due to hydrothermal oxidation of the silicon nitride by the yttrium hydroxide. Although the process worked well on small batches (4 kg), on scaling up to 30 kg batches there were yttrium hydroxide agglomerates (100 μ m) in the product found to be caused by improper control of the salt concentration, causing supersaturation, Figure 2-2. By modifying the process to obtain a constant salt level throughout the precipitation process, the agglomerates were eliminated, Figure 2-3. However, difficulties were then encountered in concentrating the slurry. Due to time restraints the precipitation method was abandoned in favor of a more reproducible comilling process.

C-Series Process

The co-milled process (C-Series) was developed in response to scaleup problems with the W-series and became the standard process for the program. The silicon nitride powder was co-milled with a yttrium oxide powder, Figure 2-4. Significant foaming was initially encountered and eliminated with suitable surfactants. The surfactant system was complicated by the two component system. Filtration was more difficult as compared to the W-series in which only silicon nitride is filtered. The final rheology of the slurry was much different from the W-series, with a much lower viscosity being obtained at a given solids loading.

Figure 2-1: Process Flow Chart, W-Series

Figure 2-2: Baseline Precipitation

Figure 2-3: Modified Precipitation

Figure 2-4: Process Flow Chart, C-Series

PROCESS CONTROL

SQC Control Charts

Shewhart control charts were employed for tracking mean and variance of key variables under optimized conditions for which upper and lower limits were established. Table 2-1 shows the variables initially monitored and those added during the program in response to issues encountered in control of downstream process properties. A statistical quality control software package was implemented with the ability of providing programmed indication of Out-of-Control (OOC) conditions (SQPack/Plus, PQ Systems, Inc., Dayton, Ohio). Control limits ($\pm 3\sigma$) and specifications were established for the milled powder properties.

Table 2-1: Process Control Variables

ORIGINAL	ADDITIONAL
Oxygen	D10, D90
Surface Area	pH
Yttria	Viscosity
D50	IEP, Cast Rate
Fracture Toughness	Specific Gravity
	Packing Density

In order to monitor the powder processing independent of forming issues, aqueous milled powder was freeze dried, screened, preformed and CIP'd as tiles. Tiles were HIP'd for each batch of powder prepared. Test bars were machined and tested for strength and fracture toughness. Fracture toughness eventually became a key control parameter for the powder, Figure 2-5. Fracture toughness values were higher for this water milled process than baseline properties (6.3 vs 5.4 MPa $\sqrt{m}$). Packing density was another measurement that was obtained independent of the forming process using a preformed and CIP'd pellet. Samples of the powder from each of the powder lots were archived for future reference.

Quality Assurance

Calibration, standards and sampling of powder specimens have been discussed in Appendix 1. A detailed SOP was written for the powder processing operation. The analytical methods employed to analyze powder and slurry properties are listed in Table 2-2.

Figure 2-5: Fracture Toughness of Qualification Tiles

Table 2-2: Powder Characterization Techniques

MEASUREMENT	TECHNIQUE
Particle Size	Sedimentation (Sedigraph 5101) Laser Scattering/(Malvern) Photon Correlation Spectroscopy
Surface Area	BET Gas Adsorption
Cation Impurities	Emission Spectroscopy
Anion Impurities	Ion Chromatography
Oxygen Carbon	Leco IR Adsorption
IEP/Conductivity	Acoustophoretic Mobility (Pen Kem 7000)
Yttria	Induction Coupled Plasma
Surface Chemistry	ESCA FTIR
Moisture	Karl Fischer Titration
Phases	X-Ray Diffraction NMRS (Xstallinity)

Milling Control

Lot-to-lot as received powder variability required adjustment of milling conditions to achieve the same average particle size. Sedigraph

measurements were obtained at different times in the milling cycle. Figure 2-6 shows how the average particle size varied lot-to-lot at the beginning of the milling process and how by adjustment of the milling conditions a consistent final milled average particle size was achieved. Solids content also allowed for control over the size distribution, with higher solids contents resulting in a broader size distribution, with a decreased D10 (% finer than).

Figure 2-6: Chart for Particle Size - D50 For C-Series Mill Batches

Surface Chemistry

The casting rate characteristic of each batch of slurry was determined by pressure casting a 3" diameter disc and measuring the thickness as a function of time. The slope of the plot of thickness squared vs time was taken as an indicator of casting rate. Figure 2-7 shows the casting rate slopes obtained for each slurry batch produced from UBE powder Lots D, E and F. A slope of less than 5 indicated a slurry that would have a slow casting rate, high cast density and acceptably low warpage during HIP'ing. Casting slopes for Lot E powder were unacceptably high, resulting in unacceptable warpage (runout) during HIP'ing. There was a somewhat narrower size distribution obtained from Lot E powder, resulting in a slightly lower CIP'd packing density, but not enough to account for the significant decrease in cast density.

The surface charge of the slurry was measured as a function of pH using both a PenKem 7000 and by Dr. Subhas Malghan at NIST using a Matec 800. The ESA (electrokinetic sonic amplitude) measurement using the Matec 800 showed the Lot E batches to possess a significantly higher isoelectric point than for Lot D batches. This was also the case for the starting Ube Si₃N₄ powders. These measurements were supported by measurement of the isoelectric point using the PenKem 7000.

In order to improve the surface chemistry, chemical rinsing and thermal treatments were evaluated. These treatments were successful on small batches (200g), decreasing the isoelectric point significantly and in most cases improving the casting behavior even relative to the Lot D untreated powder.

Figure 2-7: Casting Rate Slope for Lot D, E & F Mill Batches

FTIR analysis of the powder before and after the treatments showed a significant change in the relative amounts of silanol and amine surface species. The treatments either decreased the amine species, leaving the same silanol species or significantly increased the silanol species. Rinsing treatments (Batches C035, C036) and a thermal treatment (Batch C043) were evaluated on large batches. Only incremental improvements in the casting slope were obtained, which was supported by only a slight decrease in the isoelectric point. Further scaleup optimization of these treatments is required.

Prior to receipt of Lot F powder, several pre-shipment samples of various Ube lots were analyzed for isoelectric point and particle size distribution. The lowest isoelectric point Ube lots were selected for Lot F shipment. The milled Lot F powder was acceptable in casting rate, cast density and warpage. The isoelectric point was also acceptably low.

The oxygen content of the milled powder decreased for Lots E and F, causing the process to be out of control and being very close to the lower limit specification for oxygen. The decrease in oxygen was caused by a decrease in the oxygen content of the Ube silicon nitride powder for these lots. The need for a broader particle size distribution (coarser E03) and selection of an optimum isoelectric point resulted in the selection of the Lot F powder from a number of pre-shipment samples. The thermal treatment used for Batch C043 resulted in the oxygen content being increased to an acceptable level. Due to the effect of the Ube silicon nitride on the final milled powder properties it was determined that revised specifications are required to ensure a controlled milling and casting process. These revised specifications include isoelectric point, oxygen content and particle size distribution.

Inclusion/Agglomerate Free Product

The baseline process iteration failure origins were mainly iron inclusions resulting from the equipment used for injection molding. Iron inclusions were also a major failure origin in the baseline alcohol milled CIP'd rods. Therefore, the milling process was designed to eliminate the potential for metallic inclusions, especially iron. Features included processing within a Class 10,000 cleanroom, separation of dry powder from the milling area, use of filtered and deionized water, magnetic separation and filtration of the milled slurry, use of a closed loop system from milling to casting, non-metallic materials of construction throughout the milling and casting, high purity/low attrition HIP'd milling media of the same composition, and use of microfocus x-ray to monitor inclusions at each step of the process. The final iron level in the milled powder was <1 ppm as measured by emission spectroscopy.

Metallic inclusions from 25 to 200 microns in size were detected by microfocus x-ray, in the in-coming Ube silicon nitride powder. The frequency of inclusions did vary lot to lot, with no inclusions detected in the final Lot F powder. The final milled slurry did not possess any metallic inclusions as measured by microfocus x-ray, to within the 25 μm limit for this technique. Failure origins in some final HIP'd bars consisted of fine regions of iron silicide that were 1-5 microns in size, which linked to form a failure origin as large as 100-200 microns, Figure 2-8. These linked FeSi_x based regions are not always detectable by microfocus x-ray.

An increase in metallic inclusions as failure origins was experienced for Iteration O through R. The source was traced to a piece of equipment used in the pressure casting scaleup. This source was eliminated as well as every other potential source of metallic contamination throughout the process. The frequency of metallic inclusions detected by microfocus x-ray was immediately decreased, Figure 2-9. There were no iron related failure origins in the second half of Stage II and throughout Stage III.

Milling Optimization

The use of appropriate surfactants allowed the control of oxygen content to levels no higher than those obtained for alcohol milling. The closed loop system eliminates the need for drying and redispersion, thus decreasing the potential for inclusions and agglomerates.

A study was conducted in Stage II to determine the optimum surfactant for milling and casting. This study showed that the oxygen could be controlled, the milling rate improved and the cast density improved with alternative surfactants. However, a drying related cracking problem was experienced with the alternative surfactants. Therefore the baseline surfactant was retained for Stage III. Using alternative surfactant, the particle size distribution as measured by the Sedigraph 5100 was found to be identical to the baseline surfactant, however the surface area was significantly higher. The Sedigraph 5100 does not resolve well below 0.2 microns. A Malvern System 4700c sub-micron particle size analyzer was evaluated, but could not resolve the

differences on the as milled slurries due to the broad size distribution.

Figure 2-8: Fine Scale Iron Silicide Aggregate Failure Site

Figure 2-9: Microfocus X-ray Flaw Detection of Inclusions in HIP'ed Rods

A study was conducted to determine the effect of solids content on the vibration milled powder. Higher solids loadings were shown to decrease the D₁₀ (10% finer than) and increase the D₉₀ (90% finer than) as measured by the Sedigraph 5100. This resulted in a slightly higher packing density. The effect of solids content on milled particle size distribution provide some control over the effect of Ube silicon nitride powder particle size variability.

COLLOIDAL CONSOLIDATION PROCESS DEVELOPMENT

The colloidal consolidation (Pressure Casting) process development was performed utilizing concentrated aqueous suspensions described in the previous section. Both the precipitated (W-series) and co-milled (C-series) suspensions were evaluated for their casting behavior and resultant tensile strengths. C-series suspensions, in general, exhibited greater reproducibility and improved mechanical properties. Consequently, C-series suspension was selected to conduct all casting experimentation and optimization in the program.

Slurry Development and Characterization

The milled and concentrated batches described in the previous section were conditioned following the established SOP. SOP included sonication with an ultrasonic horn for five minutes, followed by deairing in vacuum (60 mm of Hg). In addition, the slip was characterized for agglomerate population using an agglomermeter gage. Approximately ten samples per casting batch were examined to ascertain the agglomerate population in the slip.

A comprehensive aging study was conducted for water milled silicon nitride slurry for a period of 24 days following the concentration of the milled batch. The investigation focused on establishing the cause-effect relationship involving slurry behavior and certain basic slurry parameters. Measurements of viscosity, pH, centrifuged sediment packing density and hard agglomerate size were made daily for the first 5 days, and then at one week intervals. Simultaneously, NMR longitudinal relaxation time (T₁) and spin-spin transverse relaxation time (T₂) measurements were conducted at Argonne National Laboratory. The viscosity (Brookfield, @30 RPM) of the slurry remained at 22 cp during the aging. Largest agglomerate size as measured by a gage was relatively constant at 25 μm . The slurry pH was found to increase from an initial value of 9.8 to final value of 10.4, and the packing density of the sediment (obtained by centrifuging the slurry for 30 min. at ~1000g) was found to increase from ~57 to 60.5 v/o during the 24-day aging period, Figure 2-10.

The changes in the proton NMR longitudinal relaxation time are given as a function of aging time in Figure 2-11. In general, a reduction in the T₁ value is observed with increasing aging time. During the initial stages, the T₁ demonstrates oscillatory behavior. It subsequently stabilizes at ~680 ms after 13 days of aging. The decrease in T₁ parallels the increase in the centrifuged sediment density. This suggests that dynamic chemical processes govern aging of the slip initially, reaching an equilibrium state in about two weeks. A general increase in the T₂ values is seen (1.7 - 2.2 ms), which parallels the increase in pH of the slurry. The proton exchange rate between the water molecules decreased with pH, causing an increase in the proton T₂ values.

Figure 2-10: Aging Behavior of Aqueous Slurry

Figure 2-11: NMR Aging Behavior of Aqueous Slurry

The T₁ and T₂ values of pure water are about 1500 ms. The lower T₁ values observed for the slurry indicate that the water molecules have restricted motion, presumably because they are tied up with the surface of colloidal silicon nitride particles. The T₂ values are much shorter than T₁ because of chemical exchange. Reductions observed in T₁ indicate more "ordering" of the water molecules as the slurry undergoes an aging process.

Mold Design

The nature of the density variability in a cast specimen depends upon total filtration surface area and the gate location(s) of the mold. In the initial casting work the mold provided a filtration surface all around the cavity. In the modified mold design, the filtration area was reduced and at the same time, gate locations were altered. Whereas drying cracks were frequently encountered in the early work, cast bars from the modified mold showed no cracking even under uncontrolled (ambient) drying conditions. The reduced filtration surface resulted in a single casting front as opposed to multiple fronts in the full filtration surface mold. Drying related cracking occurs where several fronts meet.

A comparison of the two mold designs was conducted on a pair of pressure cast NSF bars. One of the bars was cast using 100% filtration surface of the plaster mold, while the other had a portion of the mold surface sealed. The 10 mm diameter gage sections of the two specimens were imaged using x-ray computed tomography (CT). Four slices (each 1.06 mm thick) were reconstructed with a tomographic image size of 256 x 256 pixels. The results are represented in line profiles of the image intensity across two diameters at 90° to each other, Figure 2-12. The profiles display raw pixel grey level data. While smoothing would aid interpretation, there nonetheless is a significant distinguishing characteristic of the two CT scans apparent in these raw data, and it involves the intensity at the center of the profiles (bar centerline). This location is a point of low density for the 100% filtration case, while it is a point of high density for the partial filtration case. These results suggest the possibility that the mechanism of cracking during drying of as-cast bars in the 100% filtration case involves the low density core indicated by the data. Low core density will help generate tensile hoop stress on the surface of the bar during drying and hence contribute to the likelihood of longitudinal cracking.

Figure 2-12: Evaluation of Mold Design by Density Profile Measurement Using Computed Tomography

Density Uniformity Control During Filtration

Density gradients in the cast body are generated during the pressure filtration process corresponding to permeability changes within the cast layer. A technique was developed using programmed pressure profiles to mitigate this density non-uniformity problem as described below.

Figure 2-13 illustrates the non-linear casting rate that occurs under a fixed pressure when pressure casting tensile bars. The plot was developed from cast layer thickness data during casting at constant pressure level (0.07 - 0.42 MPa). The nonlinear casting rate implies an inherent density gradient in the cast cake. The cast bars from these experiments when densified showed preferential bending. By applying a programmed pressure schedule during casting the cast rate can be linearized, as is approximated in Figure 2-14. Bars cast according to this schedule showed negligible distortion and thus suitably uniform green density.

Besides the linearity of the casting behavior, the casting rate magnitude also influences the level of density gradient. An SOP was developed to achieve the acceptable level of the casting rate to assure density uniformity within the specified limits. The procedure established a go/nogo criterion for acceptance of a slurry batch, as follows:

- A fixed volume of slip is cast at constant pressure on an established porous material.
- The thickness of the cast is monitored at fixed time increments.
- Thickness squared vs. time of cast is plotted for the slurry, Figure 2-15.
- The slope of the line is estimated using linear regression.
- If the slope of the line is found to be greater than specification (UCL, Figure 2-15), the slip is rejected.

Figure 2-13: Nonlinear Casting Rate Under Constant Pressure

Figure 2-14: Linearized Casting Rate with Programmed Pressure Schedule

Figure 2-15: Puck Casting QC for Slurry

The importance of this casting rate measure is shown by examining the effect of the casting rate slope on the total indicated run-out (TIR), Figure 2-16. TIR is a measure of the amount of warpage or bending of the tensile rod caused by the green density gradient and determines the yield during the densification stage. Runout also has a

bearing on the tensile strength, as it determines the amount of removal of the relatively low density reaction layer during the machining process, Figure 2-17.

Figure 2-16: Regression of Average HIP'ed Runout on Casting Rate

Figure 2-17: RT Strength - Runout Correlation

Casting of Net Shape Formed (NSF) Tensile Bars

In all casting experiments a well dispersed aqueous suspension of silicon nitride containing 4w/o yttrium oxide as a sintering aid was

utilized. The suspensions contained approximately 70w/o (43v/o) solids (average particle size $0.8\mu\text{m}$) and were stabilized at $\text{pH}=9.5$. The cast ready suspensions were characterized using a Brookfield viscometer. The suspensions showed a typical shear thinning behavior (Figure 2-18). As mentioned in the previous section, the ceramic suspensions used in this study were prepared using a closed loop aqueous comminution and slip conditioning procedure. Slip conditioning procedure included sonication followed by deairing.

Figure 2-18: Viscosity vs. Shear Rate for Aqueous Ceramic Suspension

Throughout the experimentation two piece plaster of Paris molds were employed having average pore size of $2.0\mu\text{m}$ (evaluated by mercury porosimetry technique). Prior to casting, all molds were preconditioned by soaking them in DI water for 3 minutes. The ceramic suspension was fed into the mold under specified pressure from the two ends of the mold cavity near the buttonhead section of the tensile bar.

Large scale NSF bar casting iterations were performed to evaluate the effects of the process variables and optimize the casting process. A program pressure profile was utilized during casting to assure linear casting rates and hence minimal density gradient. In each iteration greater than 70 NSF tensile bars were cast, dried, degassed and HIP'ed, machined, radiographed and tensile tested.

During the casting of NSF bars, some difficulty was encountered in establishing the necessary time for completion of the casting process. In some cases, overcasting resulted in shrinkage related cracking at the buttonhead radius. These forming defects are possible failure origins during tensile testing. In order to alleviate this problem, an ultrasonic (UT) based in-situ monitoring technique was developed to establish the completion time.

Ultrasonic Monitoring of the Casting Process

Ultrasonic Characterization of the Ceramic Suspension. The ultrasonic impedance of a column of ceramic suspension and a saturated cast body were established to provide baseline data needed in the process monitoring. The liquid column measured 25 mm diameter x 198 mm high. A 1.5 MHz UT transducer was placed at each end of the liquid column or cast body to measure time of flight and signal amplitude (attenuation). Results are compiled in Table 2-3.

Table 2-3: Ultrasonic Characteristics of Casting Systems

Materials	UT PROPERTIES	
	Velocity (m/sec)	Attenuation (db/mm)
Water	1500	0.0
Slip (70 w/o solids)	1385	0.154
Cast Green Saturated Bar	1516	0.094

As expected, the attenuation in the ceramic suspension exceeds that of pure water. Sound velocity in the cast body is similar to that in water as all its pores are fully saturated. For a similar reason, the impedance in the cast body is also lower than that measured in the suspension. The ultrasonic characteristics of the slurry and the cast body established from these experiments were used to interpret the wave forms during in-situ monitoring of the casting process.

In-Situ Monitoring of the Filtration Process Casting experiments were performed in a two piece plaster mold. The mold cavity shape was that of a buttonhead tensile bar. Figure 2-19 shows a schematic of the mold cavity along with the location of the UT transducers. Two transducers (1.5 MHz), one at each end of the mold cavity, were placed such that their active faces were flush with the end of the cast tensile bar button heads. The transducers were fixtured in the mold to assure positive contact with the cast bar throughout the experimentation and to prevent being pushed out of the mold under the applied suspension pressure. The mold cavity was fed from two gates located at the two ends of the bar near the buttonheads.

The mold cavity was pressurized with the suspension at 0.14 MPa (20 psi) and the casting process was monitored by the attenuation of the ultrasonic signal. The ultrasonic signal was transmitted from one end and received at the other end of the mold cavity. Both the amplitude and the time of flight were monitored throughout the experimentation using a personal computer, Figure 2-19. A computer algorithm was designed to acquire maximum signal amplitude and the corresponding time of flight at regular time intervals.

Through transmission

- a. Amplitude
- b. Time of flight

Figure 2-19: Ultrasonic In-Situ Monitoring of Tensile Bar Casting

As suggested by Figure 2-19, as the cast layer thickness increases, the received signal amplitude increases while the time of flight decreases. This trend continues until the completion of the casting process. Upon completion the amplitude and the time of flight achieve their highest and lowest values respectively. This may be explained by the fact that at this point the cavity is completely filled with the powder and the interstitial spaces are fully saturated with the liquid (water), thus providing highest conductance path for the UT signal. Beyond this point, the suspension supply to the cavity ceases due to the casting of the gate. However, because of the continued drainage of the pore fluid through the plaster mold, water content in the cast body decreases causing precipitous drop in the UT signal amplitude. At this point the cast body should be removed from the mold. If, on the other hand, the drainage process is allowed to continue (overcasting condition), the cast part begins to shrink non-uniformly inside the mold resulting in undesirable cracking, specifically in the transition regions (as would be the case for a turbocharger rotor casting).

Typical wave forms of the received signal as a function of the casting time are shown in Figure 2-20. In the beginning ($t=t_1$) the signal is transmitted through the suspension only and a single wave signature appears on the oscilloscope screen. As the casting progresses ($t=t_2$), the signal is transmitted both through the suspension and the cast layer and two separate signatures appear. With further progress in casting ($t=t_3, t_4$), more and more signal is carried through the cast

layer and hence the cast layer signature amplitude eventually exceeds that of the suspension. With increasing signal amplitude the corresponding time of flight decreases. Finally, the suspension signature disappears ($t=t_5$) leaving a single signature representing the cast body.

Figure 2-20: UT Signal Characteristics as a Function of Casting Time

The results have been reproduced for various applied pressures and suspension concentrations thus providing a simple and yet effective way to monitor and control the casting process.

Comparison of Ultrasonic and Physical Casting Rate Data. Cast thickness physical measurement data are plotted in Figure 2-21 with the UT amplitude data from Figure 2-19. These data correspond to the casting experiments performed at a fixed applied pressure of 0.14 MPa (20 psi). The casting kinetics data from physical measurements are in reasonably good agreement with the UT data suggesting that the UT amplitude could be utilized as a feedback signal to adjust the applied pressure and hence control the casting rate for an intelligent processing methodology.

INJECTION MOLDING PROCESS DEVELOPMENT

Injection molding was the initial process in the program and supplied baseline tensile strength data. With reference to Figure 2-4, the process steps subsequent to slurry concentration were as follows: freeze drying, compounding, injection molding, de-waxing, pre-sintering (de-gas) and HIP'ing. Here compounding, mold design, molding process optimization, and dewaxing will be addressed.

Figure 2-21: Comparison of Casting Rate Prediction from Ultrasonic (B) and Physical Measurement (A)

Compounding

The molding compound was prepared by mixing the powder with a thermoplastic based binder system under high shear. Molding compound was fully characterized by measuring the rheology (viscosity as a function of shear rate and temperature), thermal conductivity, P-V-T (pressure-volume-temperature) correlation, density and specific heat, as described below.

Mold Design

In order to optimize the mold design, two techniques were used. The first was experimental including experimental design and analysis of the molded parts using both destructive and nondestructive methods. A second task was conducted in parallel to the experimental work which involved finite element modeling (FEM) of the mold filling process. The FEM modeling work was conducted in collaboration with CAE Technology Inc., Ithaca, New York. Two different gate designs were evaluated experimentally which are designated as end gate, "G2", and fan gate, "G3" as shown in Figure 2-22. The experimental work provided both information on initial conditions necessary for the FEM work, and later, confirmation of the results generated by the modeling.

The experimental work was carried out using a mold with a single tensile bar cavity. Factorial experimental designs were utilized in order to evaluate both mold design as well as molding parameters. All tensile bar specimens molded with various combinations of molding parameters were fully characterized by microfocus X-ray for internal voids. The NDE data from the two gate designs suggested little difference between the two designs regarding void density.

Single Flow Front For End Gate

Multiple Flow Fronts For Fan Gate

Figure 2-22: Injection Molding Melt Flow Velocity by FEM

The finite element modeling required two steps: materials characterization and mold filling simulation. The materials characterization determined the density, specific heat, thermal conductivity, rheology and pressure-volume-temperature behavior of the ceramic molding compound. The rheological behavior is plotted in Figure 2-23. Table 2-4 summarizes the remaining thermal and physical properties of the material.

The material properties, along with the initial molding parameters determined experimentally, were used to conduct the computer simulations for mold filling and packing. The two gate designs, G2 and G3, were modeled in varying sizes. Preliminary analysis indicated that the end gate should give better results based on a more uniform distribution of shear rates during filling of the part. The fan gate showed a tendency for the gate to freeze off in certain areas, resulting in a split flow of material, resulting in the possibility for air entrapment during the filling. Further analysis confirmed that the end gate, with the proper speed profile, would yield a nearly consistent (single) melt front velocity (Figure 2-22) as compared to multiple melt fronts for the fan gate design. Multiple flow fronts could result in fold lines which could serve as internal crack sites after dewaxing.

Molding Process Optimization and Control

A Taguchi-based experimental design was employed to optimize the molding parameters. All molded parts were examined by microfocus x-ray to establish frequency and size of molding related voids. From this study, injection pressure and barrel temperature profiles were found to be the significant process parameters. Total void volume in the tensile

bar is plotted as a function of the two molding parameters in Figure 2-24. This contour plot indicates that the optimum (minimum void volume) condition is achieved at intermediate temperature and pressure profiles.

Table 2-4: Ceramic Molding Compound Material Property Data

Density - Instrument: Capillary Rheometer (melt)			
State	Temperature (°C)	Density (g/cc)	
Solid	23	2.287	

Specific Heat - Instrument: DSC		
State	Temperature (°C)	Specific Heat (J/g °C)
solid	80	1.14
melt	100	1.191
	Tg = 92	

Thermal Conductivity - Instrument: K-System			
State	Temperature (°C)	Press Bar	Thermal Conductivity (W/mK)
melt	90	0	0.35

Figure 2-23: Rheological Properties of Injection Molding Compound

Figure 2-24: Radiograph Void Volume as Function of Molding Parameters

Approximately 240 tensile bars were molded in a two cavity mold, using the optimum molding conditions described above. Since the two cavities are symmetrically located inside the mold, the kinetics of mold filling for each cavity follow that observed in the single cavity mold. All bars were weighed, measured and examined by microfocus X-ray. The variation in weights and lengths was found to be 0.2% and 0.3%, respectively.

Microfocus X-ray examination results were also used to develop a flaw population histogram describing soundness of tensile bars. Figure 2-25 shows total number of flaws (voids and inclusions) observed in all 240 tensile bars at various regions of the bars. An important point to notice here is that the buttonhead farthest away from the gate shows higher frequency of flaws possibly due to incomplete mold filling. The high frequency of flaws observed in the gage section may reflect the enhanced resolution there due to smaller cross-section. The flaws detected in the as-molded tensile bars ranged between 100-300 μ m.

A good correlation was found between the weights of molded rods and the void volume detected by NDE, as shown in Figure 2-26. This suggests that the weights could be used as an on-line control variable to monitor the process. The total void volume is a summation of individual void volumes, assuming each void to be spherically shaped.

Dewaxing

The dewaxing step involved heating of the molded bars in an inert environment at a prescribed schedule. Inert environment was found to be superior to the vacuum or oxidizing condition. In the inert

environment, the decomposition rate of the binder is suppressed which minimizes the blistering problem.

Figure 2-25: Total Flaw Distribution in 240 As-Molded Tensile Bars

Figure 2-26: Part Weight Correlated to Radiographic Void Volume

HOT ISOSTATIC PRESSING

This section summarizes the HIP process and microstructural development. Comparing the effect of powder processing and forming modifications on strength and strength distribution required the reproducibility of the HIP cycles. Uniform densification was important to eliminate this operation as a source of strength variability. Based on the results of an experimental matrix, the HIP cycle was modified to optimize the toughness obtained in the tensile rods.

In addition to property uniformity, HIP loading was maximized to minimize the number of HIP runs required for production of Stage III tensile rods. Overall HIP yield in the vicinity of 80-85% was achieved in the program.

HIP Process Development

During Stage I and through part of Stage II of this program, HIP loading procedures included the use of fixtures to support the tensile rods. The procedure resulted in low loading capacity and poor yields. The HIP capacity with an alternative loading/fixturing procedure was increased from 15 tensile rods to a capacity of 30 tensile rods. The HIP procedures with standard and alternate loading were compared using tensile rods from the same batch. The improved yield and density of the alternate approach are seen in Table 2-5.

Table 2-5: Comparison of HIP Procedures

Mill Batch	Cast Batch	Loading	Density(g/cc)	Yield(%)
CO13	N	Standard	3.178	43
CO13	N	Alternate	3.211	86

Four HIP runs verified the alternative HIP procedures and the results are summarized in Table 2-6. The overall yield of 86% demonstrates the viability of these procedures. The criteria for an acceptable tensile rod require an unbroken component with at least 99.5% theoretical density. The process yield control chart in Figure 2-27 shows that the HIP procedure is reproducible. The low yield in the July 12th HIP run was caused by a thermocouple failure. The overall HIP process yield is approximately 83 percent. These procedures were followed as SOP for the remainder of the program. Further HIP process yield improvements would be feasible through fine tuning of the HIP process and better green microstructure uniformity.

Table 2-6: Summary of HIP Results

Mill Batch	Cast Batch	Density(g/cc)	Yield(%)
CO13	N	3.211	86
CO14	O	3.219	100
CO14	O	3.219	66
CO15	P	3.211	89

Microstructural Development

The fracture toughness of NCX-5102 is a critical factor in determining the tensile strength of the material. In Stage II the fracture toughness variability was dependent on the reproducibility of the HIP cycle. The fracture toughness variation for Batch V is shown in Table 2-7. The three HIP cycles of Table 2-7 had identical temperature and pressure profiles.

The HIP silicon nitride grain size, toughness and strength dependence on densification temperature, time and pressure were studied in a matrix of experiments. The following conclusions may be drawn from these sets of experiments. Temperature has a very significant effect on toughness. Time at temperature also has a significant effect on toughness. The level average toughness for temperature and time are plotted in Figure 2-28. The effect of temperature and time are significant at a 95 percent confidence level.

The mechanical property trends were correlated with the final microstructures. Two measurements were made to describe the microstructure. First, the grain thickness was estimated from 5000X micrographs of the etched microstructure. The thickness of hexagonal or rectangular shaped grain cross sections that intersected lines drawn across the micrographs were recorded. The resulting thickness distributions should approximate the actual β silicon nitride thickness distribution. Figure 2-29 is a lognormal plot of the grain distributions at 1840 °C for various soak times. As is obvious from Figure 2-29, grain coarsening occurs at 1840°C with time. Along with the increasing average grain size, the frequency of fine beta grains decreases.

The second measurement attempted to characterize the grain aspect ratio. The length and thickness of rectangular grains that intersected lines drawn across 2500X micrographs were tabulated. The distribution of aspect ratio as a function of grain thickness is shown in Figure 2-30. The aspect ratio increases with decreasing thickness. The minimum aspect ratio appears to be 4 for any grain thickness. The high aspect ratio grains tend to be associated with grain thicknesses $<0.6 \mu\text{m}$.

An additional microstructural parameter, namely, aspect frequency, was also computed. The aspect frequency is the number of grains measured with an aspect ratio greater than 4 divided by the total lineal distance of the lines drawn across the micrographs. This is somewhat arbitrary, but has a basis in toughening theory and microstructural observations of the HIP silicon nitride. The main toughening mechanism in HIP silicon nitride is assumed to be crack deflection. Deflection models predict toughness is dependent on volume fraction of rods¹. The aspect frequency is considered analogous to the volume fraction of rods.

Figure 2-27: HIP yield during Stage 2 using the HIP loading procedures without fixtures.

Table 2-7: Toughness Variability Observed with Batch V

HIP Cycle	Fracture Toughness (MPa m ^{1/2})
August 1	6.51
August 7	5.85
August 9	5.73

Figure 2-28: Toughness Moving Average for Stage 2

Figure 2-29: Lognormal Plot of B Silicon Nitride Grain Thickness Distributions After HIP at 1840°C for Different Soak Times.

Figure 2-30: Plot of Aspect Ratio vs. Grain Thickness

An ANOVA analysis of fracture toughness included grain thickness, aspect ratio, and aspect frequency as factors. The strongest correlation existed between toughness and the aspect frequency, Figure 2-31. The correlation coefficient was measured to be 0.97. At an aspect frequency of 0.0 the toughness is approximately 5.12 MPa $\sqrt{m}$. Because the aspect frequency counts only those grains with an aspect

ratio above 4, these results indicate that a toughness of $5.12 \text{ MPa } \sqrt{\text{m}}$ is expected with an aspect ratio of 4. Stronger correlation between and aspect frequency as compared to the grain thickness indicates that the principle toughening mechanism is crack deflection in HIP silicon nitride with 4% yttria. In the deflection models by Faber and Evans¹ the toughness increase was dependent on the volume fraction of fibers and fiber aspect ratio. The fiber diameter was not a factor in the crack deflection model. An example of the microstructure difference between high and low toughness materials is shown in Figure 2-32. Higher frequency of high aspect ratio grains for high toughness HIP condition as compared to low toughness HIP condition is obvious from Figure 2-32.

Figure 2-31: Fracture Toughness vs. Aspect Frequency

Figure 2-32: High Aspect Ratio, High Toughness Microstructure (top)
Compared to Low Toughness Microstructure (2500X)

The HIP condition yielding high aspect ratio microstructure and corresponding fracture toughness ($6.26 - 6.6 \text{ MPa } \sqrt{\text{m}}$) was adopted as the standard process cycle for all Stage III tensile bars.

REFERENCES

1. K.T. Faber and A.G. Evans, "Crack Deflection Processes - I. Theory," *Acta.Metal.* 31 (4) (1983).

APPENDIX 3: DEVELOPMENT AND APPLICATION OF NDE METHODS

Several NDE methods were employed during the program to monitor the process, generate flaw population data, correlate these data to parameters of the unit operations and feed back the information for process improvement. Separate specialized reports have been written on the work performed in collaboration with subcontractors using ultrasonics^[1], magnetic resonance imaging^[2], computed tomography^[3], and residual stress^[4] analysis. In-house NDE R&D efforts concentrated on microfocus radiography (MFX) and liquid dye penetrant (LDP) methods and highlights of this work are discussed below.

The initial task was to develop the techniques for application to various steps of the process. The detection capabilities of each NDE technique were determined quantitatively with appropriate reference standards which were prepared at NRDC.

TECHNIQUE DEVELOPMENT

Reference specimens were generated to determine the detection capabilities of the various NDE techniques. These specimens were used for the in-house NDE techniques as well as for the NDE pursued by the outside subcontractors. The reference specimens were prepared with defect types commonly encountered in samples from the various processing steps.

High density inclusions in the form of Fe particles were seeded into Si₃N₄ specimens of constant thickness (tiles) as well as in tensile bars. The tiles were seeded with 75, 100, and 165 μ m Fe particles. Iron particles of 20, 50, 100 and 200 μ m were seeded in the tensile specimens. The Si₃N₄ powder was mixed with various weight percentages of seeds precalculated to give a total defect number per sample. The mix was then CIP'ed into tiles and rods. Green, presintered and HIP'ed samples were prepared for the study. Green and dense Si₃N₄ samples of both geometries were used for detection sensitivity measurements on the microfocus x-ray unit.

Voids were simulated through the use of polymethyl methacrylate (PMMA) particles which were seeded into green tensile bars. The procedure for adding PMMA seeds was identical to that followed for the Fe inclusions. PMMA spheres of 20, 50, 100 and 200 μ m were uniformly distributed into the samples. Voids were simulated by decomposing the spheres under suitable temperature and vacuum. Detection sensitivity of voids in green cylindrical samples was determined by microfocus radiography using these samples.

Probability of detection (POD) at 95% confidence level was determined using the above seeded reference specimens. In the HIP'ed state Fe inclusions as small as 20 μ m were detected at lower bound probability of detection (P₁) of <0.2 (thickness sensitivity <0.3%); while at thickness sensitivity of >2.3%, P₁ = 0.97. In both the green and presintered state P₁ > 90% values were obtained for thickness sensitivity > 2%. Minimum Fe particles detected were around 20 μ m (P₁ around 0.20). Point estimates of the probability of detection were higher for HIP'ed Si₃N₄. In green samples, a 2% thickness sensitivity was achieved for lower bound probability of detection >90%.

Microfocus detection data on simulated voids yielded $P1 > 95\%$ for thickness sensitivity of 5% and higher for both presintered/ green Si_3N_4 samples. In the green/presintered state, voids as small as $100\text{ }\mu\text{m}$ were detected at low $P1$ (<0.2).

Specimens containing known density gradients were prepared in green and dense cylindrical samples. Three Si_3N_4 powders having different particle sizes were CIP'ed together to produce green rods with density gradients of 2, 6 and 8%. The gray level differences between the different density zones were easily identified by microfocus radiography. Density gradients were formed in dense Si_3N_4 samples by varying the amounts of sintering aid in three powders and then CIP'ing a compact from the powders. The dense compact had three distinct density zones with densities differing by 1, 2 and 3%. The samples were machined symmetrically and x-rayed. The three density zones were clearly detected by microfocus radiography, validating this approach of density gradient evaluation.

Agglomerates were seeded in both loose packed Si_3N_4 powder as well as in Si_3N_4 slips for detection studies. The agglomerates were classified from spray dried Si_3N_4 powder into different size fractions using steel sieves. Agglomerates were sized to 400, 140, 100, 60 and $40\text{ }\mu\text{m}$. The agglomerates were seeded into either a 8 cm^3 container of Si_3N_4 powder having a particle size of $< 20\text{ }\mu\text{m}$ or a 8 cm^3 container of a submicron colloidal slip. The container was half filled with either dry powder or slip, seeded with the agglomerates, then the remainder of the vial was filled with slip or powder.

The agglomerates were successfully detected in both the slip and powder. The detection limits of agglomerates in loose packed Si_3N_4 powder was $60\text{ }\mu\text{m}$ (2.4% thickness sensitivity) compared to $100\text{ }\mu\text{m}$ (4% thickness sensitivity) in Si_3N_4 slurry. The same size container was used during the program to analyze powders and slips for agglomerates.

A standard procedure was developed to detect cracks using fluorescent dye penetrant on cylindrical Si_3N_4 reference samples. Cracks were introduced using the Vickers indentation technique. Indent loads of 2.5 - 40 kg produced cracks varying in length from 14 - $220\text{ }\mu\text{m}$ which were measured using optical/SEM microscopy. The samples were liquid dye penetrant tested with a post-emulsifiable penetrant with level IV sensitivity. The technique was optimized until crack lengths as small as $14\text{ }\mu\text{m}$ could easily be detected. The crack length measured with the SEM was compared to that measured from LDP and results are plotted in Figure 3-1. The cracks measured with LDP were approximately $20\text{ }\mu\text{m}$ larger due to bleed out of the penetrant.

Film digitization and image processing capability was developed to quantify flaw populations in tensile specimens. The most useful feature was found to be contrast enhancement using gray level slide/stretch algorithms (adaptive thresholding). Gray level thresholding of a digitally enhanced image at selected areas on the radiograph has allowed counting and sizing of features such as metallic inclusions. This technique worked very well on radiographs whose background had an intrinsic variation due to variation of thickness. Background subtraction techniques were very useful in the identification of voids near the edge of the sample. Due to gray level differences in digital images of radiographs, only small areas of interest could be analyzed at

one time. These gray level non-uniformities are caused by non-uniformity of the beam intensity and the unevenness of the illumination when capturing the image. For these reasons, it was very time consuming to analyze the entire radiograph and to perform automated counting of the flaws.

Figure 3-1: Comparison of Vickers Indent Crack Length Measurements, LDP vs. SEM

Experimental design was adopted to optimize the film exposure conditions so maximum contrast could be achieved to improve the detection sensitivity. It was found that the use of fine-grain films at particularly low values of excitation voltage and current gave the optimum contrast/resolution. At low energy levels, the absorption coefficient difference between Si_3N_4 and Fe differs by a factor of 20. Several types of anodes (Mo, Fe, Cu) were evaluated but no beneficial advantages were seen over tungsten in detection capabilities. Mating surfaces of Si_3N_4 were made to conform to the cylindrical shape of the tensile rod. This was intended to offset the thickness gradient found in cylindrical samples, but provided no practical advantages. The combination of low tube current and high filament current proved to provide the best resolution due to less geometric unsharpness. Even though low energies were utilized, the use of thin filters vastly improved definition and increased edge detection on cylindrical samples by as much as 27%.

INJECTION MOLDING PROCESS NDE SUPPORT

Microfocus radiography was instrumental in developing the injection molding technique. As-received Si_3N_4 powder, binder, compounded mix, pelletized mix, green NSF bars, debinderized/presintered NSF bars and HIP'ed NSF bars were all analyzed by microfocus radiography

for the identification of flaw populations.

The binder used in the injection molding mixes was evaluated for high density inclusion contaminants, since such binders are manufactured for the plastics industry where these types of flaws are of no concern. The binder "D" used in the baseline iteration was processed through a set of filters and then radiographed at 10x magnification for detection of inclusions. A series of 9 experiments were carried out using a variety of filter set-ups. The final filter system tested yielded a factor of 10 reduction in the number of inclusions.

Compounded and pelletized mixes were also examined by microfocus x-ray for the presence of high density inclusions. These types of inclusions are in part products of wear from the processing equipment. The compounded mix was prepared by rolling it into a flat disc (pancake) before examining it. The pelletized mix was examined in the form of 5 mm diameter pellets. The compounded and pelletized mixes were both found to contain Fe inclusions in approximately 30% of the samples analyzed. The data on size distribution and frequency of inclusions for the compounded and pelletized mixes are shown in Figure 3-2. Inclusions from 35 - 400 μm were detected in the compounded and pelletized samples.

Figure 3-2: Metallic Inclusions Detected by MFX Radiography in Injection Molding Process

Microfocus film radiography of injection molded, debinderized and presintered tensile rods was performed. The radiographs were taken of the entire tensile rod at 2X. Each set of rods was shot at two angles (0, 90 degrees) to allow determination of whether defects were surface/near surface or bulk and to also ensure that those defects unfavorably oriented to the x-ray beam at one angle were detected.

At the early stages of development in the injection molding sequence, microfocus x-ray was used to set the molding parameters. Process parameters such as temperature, pressure, gating of mold, etc. were analyzed by examining the flaw population. For example, three different size feed orifices to the mold (D7, D9, D11) were evaluated by examining the void population in the molded rods. The orifice size chosen was based on the radiography data. Microfocus film radiography

evaluation of the as-molded tensile rods of the first iteration found an average flaw indication per sample of around two, which represented a significant improvement over earlier molding experiments which had average flaw per sample values closer to six.

There were approximately 300 injection molded rods x-rayed in the green state. The majority of the flaws were voids located in the buttonhead section of the rod. The other prominent flaw population was high density inclusions (Fe) found predominantly in the gage section. Nearly 57% of the rods tested had detectable voids and 45% of rods had inclusions. The average void size was $>500 \mu\text{m}$ and the size range of the inclusions was $200\text{--}500 \mu\text{m}$.

In the HIP'ed state, all tensile rods were 100% examined by microfocus x-ray and liquid dye penetrant. Film radiography was performed in the gage area at a magnification of 2X. All the liquid dye penetrant examinations were at 1-40X magnification on the entire test specimen. The liquid dye penetrant testing was done using a level III fluorescent post emulsifiable penetrant. The emulsification step was carried out with the hydrophilic process. A total of 94 HIP'ed rods were evaluated with NDE. Inclusions (Fe) were determined to be the major flaw population. Over 70% of the rods examined were found to contain inclusions with an average size of $200 \mu\text{m}$. Only 1% of the samples tested had voids suggesting HIP'ing healed the porosity observed in the green state. Figure 3-3 illustrates the size distribution of the inclusion flaw population for iteration 1. The major flaw population detected by LDP were cracks in the buttonhead section of the tensile specimens. A few of the specimens that had cracks detected by LDP were x-rayed to confirm whether or not it would be detected by this technique. This test was performed on 35 samples, and in every case, LDP results correlated with microfocus x-ray. The cracks seen in the buttonhead were not considered detrimental if they were not in the vicinity of the buttonhead radius where the bar is gripped for testing. Figure 3-4 is an example of a crack detected by LDP in the buttonhead region of the rod. A total of 47 rods had cracks that were potential failure sites. The other flaw population observed with LDP was machining damage. Figure 3-5 is an example of the type of machining damage observed in the transition section of a tensile bar.

Figure 3-3: Relative Frequency of Metallic Inclusions Detected in HIP'ed Injection Molded NSF Bars

Figure 3-4: Buttonhead Radius Crack (14 mm) Detected by LDP

Figure 3-5: Machining Damage in Transition Region of NSF Bar Detected by LDP

Several mini-iterations (20-25 rods) were carried out after the first baseline iteration in order to refine the injection molding process. This was pursued in an effort to reduce the size and frequency of the flaws as well as improve on the overall mechanical properties. Early experience had voids concentrated at one end of the mold in the buttonhead section of the rod. Injection molded specimens from mini-iteration Batches I and L were radiographed as-molded. Batch L was produced using binder which had been screened for inclusion control. Furthermore, on the basis of void and crack frequency observed in Batch I specimens, molding parameters were adjusted for Batch L. Radiography confirmed that the adjustments were successful since these defects were greatly reduced relative to Batch I, Figure 3-6.

Figure 3-6: Void Frequency and Distribution in As-Molded NSF Bars.

Figure 3-7: NDE/Fractography Inclusion Size Comparison

Inclusion population data gathered by microfocus x-ray were compared to fracture origin data collected with the aid of SEM. Flaws found by NDE before testing were compared to the critical flaws identified post-mortem by fractography/SEM. Flaw size at the failure origin of those rods which was identified by both techniques is plotted in Figure 3-7. The plot suggests reasonable correlation between the flaws measured by NDE and the fractography data.

COLLOIDAL CONSOLIDATION - BASELINE ITERATION - NDE SUPPORT

Pressure cast samples were analyzed by microfocus x-ray at all stages of processing. In the early stages of casting development, a preponderance of voids in green NSF bars was identified as a major quality problem. Radiography was used to monitor the effectiveness of casting procedure alternations by tracking the decrease in void population at each state of development.

The predominant defects in the green samples were voids which had an average size of 375 μm . Voids of this size or smaller were no longer evident after HIP'ing. Inclusions in the 100 μm size range were the major flaw type detected in HIP'ed samples. Film microfocus radiography was also used extensively for evaluation of density variations within NSF bars. Cross-sections of green NSF rods were radiographed to establish how density gradients and also casting fronts develop as a function of casting parameters such as filtration surface, mold material, etc.

The size distribution of inclusions for both the injection molding and pressure casting baseline iterations is plotted in Figure 3-8. As illustrated, the average inclusion size found in pressure cast samples was 100 μm compared to 200 μm for injection molded samples.

Figure 3-8: Inclusion Size Frequency in HIP'ed NSF Bars From Injection Molding and Pressure Casting Baseline Iterations

STAGE II PROCESS OPTIMIZATION NDE SUPPORT

Specimens from all stages of processing were examined by microfocus radiography during Stage II in order to monitor the process. This includes all processing steps from the starting powder to the final machined NSF bar. Liquid Dye Penetrant was used as a surface analysis tool for the identification and measurement of surface damage on HIP'ed/machined specimens. Stage II was also used to further optimize the NDE techniques for different specimens at each stage of processing. The techniques were optimized in order to achieve the best contrast and resolution between the flaw type and the bulk material.

As-Received Powder

As-received UBE powders were analyzed by microfocus radiography for the presence of metallic inclusions. At the beginning of Stage II the major flaw population governing failure were metallic inclusions. The powders were examined by microfocus x-ray since they were thought to be a contributing source to the contamination. Even though the powders meet the purity specifications, they did contain a few large particles of the impurity. Samples (40g) were taken from each barrel that contained a particular particle size (EO3, EO5, E10) for each lot of powder. This was pursued to determine whether a particular particle size lent itself to more contamination. No conclusive results were found to confirm this hypothesis. A total of 15 samples were examined from one 50 kg barrel of EO3, Lot D UBE powder. There were 10 inclusions found ranging in size from 25 - 200 μm . Samples from six 50 kg barrels of as-received Lot C UBE powder were radiographed and two samples were found to contain single 50 μm inclusions. The magnetic separation stage of the milling process was considered adequate to remove this source of contamination from the process.

Figure 3-9: Aging/Agglomeration of Slip Detected by MFX Radiography

Colloidal Suspensions

Colloidal suspensions from mill batches C011 - C029 were examined for the presence of agglomerates and inclusions. The slip was transferred into 33 cm³ plastic containers and examined at 10X using microfocus radiography. The evaluations were performed during the period that the casting operation was being conducted (within hours of milling). Agglomeration was found to occur with aging of the slip. Samples were radiographed 1.5 - 2 weeks after slip preparation and agglomerates 100 - 500 μ m in size were detected, Figure 3-9. These findings prompted a change in the casting SOP to require fresh slip for the casting process. No agglomeration was observed in any of the slips during Stage II when examined within 72 hours of milling. Ordinarily, the casting operation was scheduled to consume the slip in 48 hours.

Presintered NSF Bars

Presintered NSF bars from iterations N, O, P, Q, S, T, U, V, X, Y, Z, and AA were examined during Stage II. MFX was used to establish casting controls as they relate to air entrapment and the resultant void defects. The examination of green specimens was performed at 4X magnification at the beginning of the program. As the average flaw size started to decrease, the magnification was increased to 9X, as was the case with iterations Z and AA. A variety of flaw types were found in the gage section of the bars, including low density pores, agglomerates, cracks, and high density inclusions. The majority of the flaws seen were low density pores or voids. Flaw population charts based upon specific flaw counts were generated for each batch of green specimens.

Figure 3-10: Void Frequency in As-Cast Tensile Rods for Casting Iterations V-AA

An automated closed loop casting unit was installed at the commencement of Iteration X. Significant quality improvement was realized as can be seen in the plot of # voids/sample for iterations V through AA in Figure 3-10. There was a reduction in void frequency from a level of 3.5 to 1.5 voids/sample. The 1.5 void/sample level of iterations X, Y, Z was reduced to a 0.5 level for iteration AA, after minor adjustments of the machinery.

HIP'ed NSF Bars

The non-destructive examination of dense samples was conducted after final machining. The HIP'ed/machined specimens were analyzed by both MFX and LDP in the gage section. At the initial stages of Stage II, all microfocus x-ray work was performed at 5X. Later, as the size of the flaws decreased, the magnification was increased to 10X for all future work.

The improvement in processing over the course of the program can be plotted in terms of flaw population data versus iteration. Figure 3-11 provides plots of average flaw size and number of flaws per sample for the first 9 iterations. The flaws include pores, inclusions and agglomerates detected in the gage length volume. The plots indicate dramatic improvement in both size and frequency which corresponded to strength improvements. Another illustration of process improvement is provided by data documenting the percentage of bars which had defects detectable by MFX. Whereas in excess of 80% of baseline iteration specimens had detectable flaws, by the ninth iteration this figure was less than 20%.

Figure 3-11: Flaw Statistics from MFX Evaluation of Iteration Samples

Approximately 50% of the NSF bars from iterations 3, 4, and 5 showed no flaw indications and as Figure 3-11 suggests, there was roughly one flaw averaging 75 μm in each of the samples which had indications.

The inclusion flaw populations for iterations T-Z are plotted in Figure 3-12 in the form of # inclusions/sample and % rods with inclusions. After Batch T was processed, iron contamination was discovered in the milling and casting equipment. The iron contamination was associated with the wear and corrosion of the metallic components. At that point, replacement components were redesigned with organic materials to circumvent the problem. As can be seen in the graph, the metallic contamination was decreased drastically. Whereas more than 50% of Iteration T rods were found to contain metallic inclusions, only 7% of Iteration Z samples were found to have these defects. The equipment wear influence on Batch T is also evident in Figure 3-11, where there was a sudden rise in the average flaw size and the percentage of rods with flaws. As more and more wear areas of the process equipment were replaced, there was a gradual decrease in the flaw population from batch T to batch X. This is a good example of how the results of NDE led to the discovery of a problem in the process equipment.

Figure 3-12: Inclusion Population Statistics During Stage II and III Iterations

Density Gradient Evaluation

During the course of Stage II, specimens from several different batches were MFX X-rayed to identify density gradients. Thin cross-sections were sliced from presintered green rods with flat and parallel faces. Specimens were x-rayed to measure the effects of different casting parameters, mold materials, pressure profiles, and filtration surfaces on the formation of density gradients. For example, an x-ray of a specimen cast in a two piece mold, where only 1/2 the mold was a

filtration surface, revealed a low density region along the drawing part of the mold. This technique was very useful in refining the casting process.

A sintered Si_3N_4 step wedge was made with steps that varied in thickness by 1% to simulate density gradients. The thickness of the wedge was approximately that of the gage section of a HIP'ed tensile rod. The wedge has 7 steps and its thickness varied from .2345 to .2500 inches. The step wedge was examined using film radiography and all steps were clearly seen as shown in Figure 3-13.

Figure 3-13: MFX Radiography Density Gradient Calibration Si_3N_4 Step Wedge

Strength-Flaw Correlation

The machined NSF bars were also examined for strength impairing flaws for correlation with fractographic analysis. A number of NSF bars from Iterations T, V and X failed from inclusions during tensile testing, corresponding to the metallic contamination that has previously been discussed. Radiographs of those specimens which failed in the gage length were used to establish a possible relationship between inclusion size and NSF bar strength. Fracture mechanics suggests the relationship

$$\sigma_f = c \frac{K_{1c}}{\sqrt{a}} \quad (3-1)$$

where the constant c represents the geometrical features of the defect

with dominant dimension a . In this case, a was taken as one-half the largest inclusion dimension perpendicular to the tensile axis which was apparent in the radiograph. A penny shaped crack would have a value of 0.89 for the constant c .

Given the flaw size from the radiograph, a predicted value of σ_f was computed for each specimen using equation (3-1) and this was compared to the actual test strength. A value of $6.2 \text{ MPa}\sqrt{\text{m}}$ was used for K_{Ic} in this computation. The value considered to be the best choice for the constant c was that value which gave a regression line which best approximated the predicted = actual line, Figure 3-14. As can be seen, although there is considerable scatter in the data, the regression line with $c = 0.65$ corresponds almost exactly to the 45° line in this plot. The value of 0.65 suggests that the effect of an inclusion in Si_3N_4 is more severe than a penny shaped crack of equivalent dimension.

Figure 3-14: Predicted vs. Actual Tensile Strength From NDE Inclusion Data and Fracture Mechanics

Optimizing X-ray Unit Performance

Several experiments were conducted to establish variations in the intensity of the x-ray beam. In order to quantify density gradients in cast specimens, there is a need to know when density variation indications are intrinsic to the sample and not due to scatter or non-uniformity of the x-ray beam. Indirectly, the intensity of the x-ray was measured over the width of beam and variations up to 15% were discovered. Two approaches have been pursued to dampen the variation in the beam intensity. Pb diaphragms were tested and found to reduce the beam intensity difference to 7%, Figure 3-15.

New tungsten targets were designed with target angles less than

45° in order to improve the gray level uniformity. With the shallower targets, the beam intensity difference was reduced to less than 5% with no effect on exposure times as is the case with Pb diaphragms.

Shadow formations have been observed on magnified x-ray film images. The shadows occur on the edge of test objects and are seen as an increase in film density. It has been determined that these shadows are due to secondary radiation produced internally in the tube head. Several types of filter material were evaluated for beam hardening and the reduction of internal scatter. One filter was found which absorbed the internal scatter and nearly eliminated the edge burnout on cylindrical samples which vastly improves the detection capabilities. A combination of filters which hardened the beam and eliminated internal scatter was found to increase the edge detection on cylindrical samples by 27%. The penalty to this approach is a large increase in exposure time at low energy levels. Another approach was to redesign the tubehead to eliminate the internal scatter. Modifications were made to the tubehead to prevent the formation of secondary radiation and the occurrence of shadows.

Figure 3-15: Intensity Variations Observed in X-ray Beam

Detection of Agglomerates in Dense NSF Bars

An investigation into the detection sensitivity of agglomerates in green and HIP'ed NSF bars was conducted. It had been previously established that agglomerates in powder or slip have the radiographic appearance of high density regions. Agglomerates of Si_3N_4 powder were produced in sizes of 100 to 400 μm (using ASTM steel sieves) and samples were taped to the surface of an 11 mm diameter green bar. The agglomerates were easily detected through the 11 mm diameter. Agglomerates less than 100 μm crumbled when being taped, so that the tests were restricted to $>100 \mu\text{m}$.

Simulated dense agglomerates were produced by crushing a HIP'ed NCX-5102 billet sample. The pieces were sized from 50 - 400 μm and as

in the green testing, samples were taped to a dense 6 mm bar. In this case, agglomerates as small as 65 μm were readily detected.

STAGE III PROCESS DEMONSTRATION NDE SUPPORT

Liquid Dye Penetrant testing and Microfocus X-ray radiography were utilized as tools to monitor the introduction of defects into the process and for the identification of critical strength limiting flaws during Stage III. Microfocus radiography was used as one of the instruments to characterize specimens from all stages of processing for in-process control. It was employed at various points of the process for detection of contaminants in the raw material and colloidal suspensions and for detection of defects in the green and final machined specimens. Liquid dye penetrant testing was used to identify and measure surface damage on HIP'ed/machined tensile specimens.

The techniques were optimized in Stage II for different specimens at each stage of processing. The gage section of green and final machined tensile specimens were radiographed at 10X magnification in 3 orientations (0° , 90° , and 135°) taken from a particular reference point. Low energy x-rays were employed for improved contrast and a thin Pb filter was used to reduce scatter and edge burnout for the cylindrical specimens. The as-cast specimens were X-rayed typically at 2X in order to see the entire sample for process evaluation. Different lots of powder and colloidal suspensions were usually examined using 30 grams of sample at 10X magnification. In all cases, a slow speed, fine-grain film was used. A post-emulsifiable, fluorescent penetrant with level IV sensitivity was used for the Liquid Dye Penetrant method. All penetrant samples were examined at 35-350X magnification in the gage area with a fluorescent microscopy system.

In-Process Inspection

At the initial stages of this iteration, the powder lots (E and F) which were to be milled during Stage III were examined for contamination before hand using microfocus radiography. This was also done for each batch of slip after the closed loop aqueous milling and consolidation steps. No contamination in the form of high density inclusions were observed in either the slip or raw powder.

As stated earlier, microfocus radiography was used as an in-process control check on the casting operation. On a periodic sampling basis, as-cast NSF green tensile specimens were radiographed immediately upon demolding. The radiographic film for these bars was immediately interpreted and the results fed back to the operations manager for a go/nogo decision. This in-process inspection technique was instrumental in detecting an air leak in the casting system. A sudden rise in radiographic void indications led to the discovery of a leak which was causing air entrapment voids in the cast specimens, Figure 3-16. Corrective actions were completed after a minor interruption in the casting operation.

MTX was also used to evaluate the effect of chemical treatment of the plaster of paris molds on the low density region that develops at the filtration surface. The study was pursued as part of the Lot E

2 of 2

powder evaluation. As mentioned earlier, Lot E powder behaved differently in colloidal casting behavior and showed a significant shift in the iso-electric point (IEP). Radiography of tensile rod cross sections clearly established that the treatment of the mold with a chemical stabilizer reduces the depth of this low density zone (from 1.2 to 0.3 mm), Figure 3-17. Cross-sections from four tensile rods cast in molds treated and untreated with a chemical stabilizer were tested in this experiment. The treatment of molds was used with Lot E powder batches.

Tensile rod cross-sections from two lots of powder (Lot D & Lot E) were x-rayed to see differences in density gradient formation. This would verify if the powders exhibit similar casting behavior. Other lots of powder tested behaved very much like Lot D so it was used as the control in the experiment. The low density region associated with the filtration surface was observed in both powders. The depth of the low density zone, as measured on 4 samples from each lot of powder, was substantially reduced on Lot D compared to Lot E, Figure 3-18. These results agreed well with the earlier findings that the Lot E powder was physically and chemically different from earlier lots.

Figure 3-16: Air-entrapment Voids in Cast NSF Bars Detected Radiographically.

Figure 3-17: MFX Data Illustrating Density Gradient Control Using Mold Treatment

Figure 3-18: MFX Data Illustrating Powder Lot Variation in Density Gradient.

Microfocus radiography was used to characterize green tensile specimens at the presinter step of the process. Approximately 4% of the specimens evaluated were removed from the process due to large voids observed in the bulk. These usually occurred in specimens cast at the end of the sequence when there was minimal slip left in the tanks.

Radiography Data for Machined NSF Bars

All tensile specimens that were HIP'ed/machined were examined by microfocus radiography and Liquid Dye Penetrant testing. A total of 322 final machined test samples were characterized by both techniques. Only 17 specimens with high density inclusions, 27 specimens with porosity, and 1 specimen with a radial crack were found with radiography. Figure 3-19 illustrates the size distribution of the 17 inclusions detected by microfocus radiography. The size of the defects was taken as the longest dimension measured normal to the tensile axis. The majority (10 of 17) of the inclusions found in the test specimens were in the 0-50 μm range. These inclusions had the appearance of glassy metallic zones which were probably formed during the HIP'ing or post-HIP heat treatment processes. The density of the inclusions was radiographically only slightly higher than Si_3N_4 and significantly lower than Fe and other high atomic number metals.

Only the specimen with the crack was rejected prior to mechanical property testing. It was the intent at the start of this program to test all specimens for mechanical properties data unless it was absolutely obvious the sample was rejectable. The three specimens with high density inclusions > 150 μm had tensile strengths of 930-1080 MPa. Post failure analysis indicated that the fracture origin of the lowest strength test sample had a Ti inclusion (40 μm x 30 μm), whereas the other two samples appeared to fail from surface amorphous regions. From standard fracture mechanics, the predicted strength for a 150 μm inclusion would be ~600 MPa. In Figure 3-20, the size distribution of the porosity is shown. Over 93% of the porosity observed with microfocus x-ray was between 40-100 μm and at the surface.

Figure 3-19: Inclusions Detected by MFX in HIP'ed/Machined Stage III Tensile Rods

Figure 3-20: Pores Detected by MFX in HIP'ed/Machined Stage III Tensile Rods

Liquid Dye Penetrant Data for Machined NSF Bars

As mentioned, the surface of all HIP'ed/machined tensile rods were characterized by liquid dye penetrant testing (LDP). The four major types of flaws observed with this technique were cracks (machining related), machining grooves, porosity, and low density areas. Nearly 38% of the specimens were found to have machining related cracks. The cracks observed were radial cracks that extended from the machining grooves. The relative frequency and size distribution of the cracks are depicted in Figure 3-21. The average size of a crack measured from the edge of the machining groove was 12 μm (see Figure 3-22). The two major flaw populations observed with LDP were surface porosity and machining damage (grooves). The porosity was present in small clusters with an average size of 20 μm . These pore clusters were made up of 1-2 μm size pores which were indistinguishable due to blotout during the LDP process. The size distribution of the porosity is seen in Figure 3-23. Micrographs of typical pore clusters are illustrated in Figure 3-24. The other major flaw type, grinding grooves, occurred in nearly 90% of the specimens. These grooves from dense machining ran parallel to the tensile direction. In many instances, either surface or subsurface cracks were associated with the grinding grooves. Figure 3-25 shows micrographs of typical machining grooves detected by LDP. The width of a machining groove was generally about 5 μm . Figure 3-26 shows images of grinding grooves detected with ultrasonics using a surface wave 100 MHz transducer. The width of the grinding grooves in the ultrasonic images is 75-80 μm . The resolution of the surface wave transducer is 70 μm suggesting that the grooves seen with ultrasonics are a compilation of grooves that are spaced less than 70 μm apart.

Figure 3-21: Machining Crack Data Detected by LDP in HIP'ed/Machined Stage III Tensile Rods

Figure 3-22: A 6 μm Wide Grinding Groove With 8-35 μm Radial Cracks (750X)

Figure 3-23: Surface Porosity of Machined Stage III Tensile Rods by LDP

Figure 3-24: Pore Clusters (13-16 μm) on Machined Surface of Stage III Tensile Rods

Figure 3-25: Grinding Grooves (5 μm wide) Detected by LDP

Figure 3-26: Ultrasonic C-scan of NSF Machined Surface Indicating 70 μm Wide Grinding Grooves

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APPENDIX 4: PROPERTY TESTING AND MICROSTRUCTURAL EVALUATION

The near-net shape formed (NSF) buttonhead tensile rod was the component used throughout the program to evaluate process iterations. Tensile testing was the primary evaluation method. Tensile rods were used to establish representative fast fracture strength distributions at room temperature and at 1370°C. Stress rupture and creep behavior were also tested using the buttonhead specimen. Fracture toughness tests were performed using 3 x 4 x 50 mm flexure bars machined either from tensile rods or from tile produced within the process iteration.

The primary purpose of the extensive tensile testing conducted in the program was to establish a comprehensive understanding of how flaw populations and process parameters influence mechanical properties. Hence, a thorough inspection strategy was followed at each step of the process to form the necessary database to establish correlations. For instance, prior to machining of the specimens density and runout measurements were conducted. After machining, dimensional tolerance and surface finish were evaluated. Also at this step, radiographic and liquid dye penetrant evaluations were conducted. The entire flow diagram for the tensile specimens from densification to post-mortem analysis is shown in Figure 4-1.

Figure 4-1: Specimen Flow Diagram for Testing and Failure Analysis.

TESTING PROCEDURES

Dense Tensile Testing

The cylindrical buttonhead tensile specimens¹ were tested on an Instron Model 8562 utilizing the Instron "Super-grip" and straight tri-split copper collet system. A double ramp loading procedure was used to test all specimens. The specimen is initially loaded to 6668 N (1500 lbs.) at 39 MPa/min (250 lbs./min). This allows time for the fully annealed copper collets to deform to the buttonhead radius of the specimen. After the initial ramp to 6668 N, the specimen is then loaded to failure at a stressing rate of 600 MPa/min.

The load train is checked before testing with an alignment tool for actuator/load cell alignment and a strain gaged tensile specimen for Instron "Supergrip" alignment. Each specimen was marked on the surface (outside the gage section) relative to its position in the tensile grips to allow location of surface failures relative to the grips, as an additional check on alignment. The diameter of the specimen was measured after failure near the fracture surface to eliminate the possibility of surface damage from the calipers prior to testing. The micro-location of the failure origin is determined (gage vs. transition) by the measurement.

Optical fractography was performed on all specimens. Following optical observations, all specimens were submitted for scanning electron microscopy, SEM, and energy dispersive spectroscopy, EDS. Low and high magnification micrographs were taken of each fracture surface and flaw origin. The EDS is performed at each origin to determine if any impurities are present. The location, type and size of each flaw were noted, measured and tabulated for database evaluation.

Procedures for tensile testing at room temperature and elevated temperature were established by testing NT154 silicon nitride cylindrical buttonhead specimens at three gage diameters. The RT and 1370°C strength data are summarized in Table 4-1. Optical fractography of the RT specimens indicated 35 of 37 specimens failed at the surface while the 1370°C specimens all failed from bulk flaws. Also approximately 20% of the RT specimens failed at the gage transition region where finite element modelling has indicated a slight stress elevation.

Table 4-1: Tensile Data From NT154 Samples

Gage Diameter (mm)	20°C			1370°C	
	Mean Strength (MPa)	Standard Deviation (MPa)	Number	Mean Strength (MPa)	Number
4.5	716	83	12	431	2
5.5	685	76	12	428	2
6.35	711	77	13	449	3

Green Tensile Testing

Fixtures were designed and an SOP developed for testing green and presintered NSF tensile bars. As-injection molded specimens were found to have mean strength at the 3.0 MPa level. The variability was found to depend strongly upon the processing conditions.

Tests were conducted on pre-sintered NSF bars processed from both the injection molding and pressure casting routes. Strengths were found to fall in the 5.0 - 8.0 MPa range for each case.

The molded specimen failure origins included agglomerates, dewaxing cracks and metallic inclusions. The cast specimen failure origins consisted of agglomerates, pores and hoop cracks formed during drying.

BASELINE TENSILE DATA

Injection Molding

The first iteration used injection molding to form NSF tensile specimens. A total of 49 specimens were tested for RT fast fracture strength and of these, 26 failed from gage section defects, while the remainder failed from buttonhead defects. The strength data are summarized in Table 4-2. The strength for the specimens which failed at the buttonhead was calculated as the stress in the gage section at the point of buttonhead failure. Also included in Table 4-2 are data for 35 flexure specimens machined from five tensile rods and tested at room temperature.

Table 4-2: Injection Molding Baseline RT Tensile Strength Data

Failure Location	Average Strength (MPa)	Standard Deviation	Range	n
Gage/Volume	506	91	327-663	17
Gage/Surface	356	201	38-629	9
Buttonhead	442	94	276-632	23
All	454	121	38-663	49
Flexure	760	159	255-965	35

The mean strength for all 49 specimens was 454 MPa with a characteristic strength of 492 MPa and Weibull Modulus of 4.2. The strength data compares well with early PY6 injection molded data² and is slightly lower than more recent data³.

Fractography established that all 23 buttonhead failures were from pre-existing surface cracks due to the injection molding process. These flaws were detected using a dye penetrant technique as part of the post-

machining inspection. Of the 26 gage failures, 17 failed from volume defects and 9 from surface defects. The defects were mainly inclusions with a few agglomerates and pores. The inclusions were either Fe, Ti, Al, Cr, Zr, Ni or a combination of these. The source of the defects was traced to the binders used as well as the injection molding equipment. The size of the flaws ranged from 100 to 500 μm .

Fracture toughness measurements⁴ performed on flexure bars machined from tensile rods resulted in an average K_{Ic} value of $5.35 \pm 0.037 \text{ MPa } \sqrt{\text{m}}$.

Fast fracture tensile testing was performed on 15 specimens at 1370°C in air and the data are summarized in Table 4-3.

Table 4-3: Injection Molding Baseline 1370°C Tensile strength Data

Failure Location	Average Strength (MPa)	Standard Deviation	Range	n
Gage	199	127	64-370	13
Buttonhead	236	---	230-242	2
All	204	118	64-370	15
Flexure	456	18	150-607	14

There were only two buttonhead failures caused by pre-existing surface cracks which were introduced during forming. Seven of the remaining 13 failed due to slow crack growth at stresses below 140 MPa, while the other six failed at stress levels in excess of 250 MPa. Also included in Table 4-3 are data for 14 flexure specimens machined from five tensile rods. As expected, the strengths are greater in flexure than in tension.

Tensile stress rupture tests were performed on five specimens at 1230°C in air at an applied stress level of 350 MPa. The times to failure were 0, 2, 5, and 20 minutes, with one specimen failing during loading at a gage stress of 278 MPa. All specimens failed in a fast fracture mode as opposed to slow crack growth. This may be explained by considering the fact that the average strengths at room temperature and 1370°C were 454 and 204 MPa, respectively. These data suggest that the applied stress of 350 MPa is very close to the fast fracture strength of this material at 1230°C. Flexure stress rupture tests were also performed on four specimens machined from tensile rods. One failed immediately and three survived 200 hours before test termination.

Colloidal Consolidation

Room temperature fast fracture strength tests were performed on 28 specimens from the baseline pressure casting iteration. In this group of specimens, eight were HIP'ed to less than 99% theoretical density. Figure 4-2 illustrates that strength falls off significantly below 99%

T.D. and for that reason the 8 low density specimens were not used in the iteration data analysis.

Figure 4-2: Strength vs. Density for Pressure Cast Tensile Rods

The tensile strength data for the 20 valid specimens are summarized in Table 4-4. There were 9 volume, 6 surface, 4 buttonhead and one unknown failure origins. The overall average tensile strength and Weibull Modulus are 709 MPa and 4.7, respectively.

Table 4-4: Pressure Cast Baseline RT Tensile Strength Data

Failure Location	Mean (MPa)	Standard Deviation (MPa)	Range (MPa)	Number of Specimens
Gage/volume	636	193	397-1010	9
Gage/surface	845	118	701- 961	6
Buttonhead	628	121	532- 810	4
All	709	174	397-1010	20*
Flexure	857	126	527-1177	60

* includes one unknown flaw origin

The tensile specimens included in the above data set were cast from two different slips (C-series and W-series) as part of a larger

matrix of experiments. Table 4-5 summarizes the strength data according to slip type. The bars cast from C-series slip show a much higher tensile strength (862 MPa) and Weibull Modulus (10.0) than for bars cast from W-series slip.

Table 4-5: Slip Comparison for Pressure Cast Silicon Nitride

Slip	Mean Strength (MPa)	Standard Deviation (MPa)	Characteristic Strength (MPa)	Weibull Modulus m	n
C Series	862	136	911	10.1	5
W Series	658	158	719	4.6	15

Fractographic analysis found that the major flaw population in this iteration was that of agglomerates. In one case, a silicon inclusion was detected within an agglomerate failure origin. In all other instances the chemistry of the failure origin was identical to the matrix as determined by EDS in the SEM (Figure 4-3). The agglomerates were found both in the volume and at the surface. It should be noted that the specimens that failed at the surface had machining damage concurrent with an agglomerate. The size range of the agglomerates at the fracture origin for the NSF bars made from C- and W-series slips were measured to be 10-25 μm and 25-100 μm , respectively, much smaller than the 100-500 μm sized defects identified as failure origins of the injection molded baseline specimens. The improved pressure cast strength data reflects the reduction in flaw size.

Fracture toughness was measured by the indentation strength (IS) technique on MOR bars machined from NSF tensile rods. The values ranged from 4.5 to 6.2 MPa $\sqrt{\text{m}}$. Powder XRD was performed on the specimens with the lowest and highest toughness values to determine the amount of retained α crystal structure. The specimen with the toughness of 4.5 MPa $\sqrt{\text{m}}$ had 64% α phase as compared to only 18% α phase for those specimens which measured K_{Ic} of 6.2 MPa $\sqrt{\text{m}}$. The toughness value measured by the indentation fracture (not IS) technique is plotted in Figure 4-4 as a function of % α phase silicon nitride for each of the iteration tensile specimens. As expected, a definite trend of decreasing fracture toughness with increasing retained α phase is apparent from the plot. These results provided strong evidence that the goal of improving reliability would require both microstructure (K_{Ic}) and defect control.

Fast fracture tensile tests were performed on four specimens at 1370°C in air with a resulting average strength and standard deviation of 361 ± 3.5 MPa. Optical fractography indicated two volume and two surface flaw origins consisting of agglomerates (same composition as surrounding matrix). High temperature fast fracture testing was also performed on 20 flexure specimens machined from tensile rods, with a resulting average strength of 575 ± 52 MPa.

Figure 4-3: Failure Origin Composed of an Agglomerate at the Site of Machining Damage.

Figure 4-4: Fracture Toughness vs. % Alpha Silicon Nitride

Stress rupture tests were performed at 1230°C in air on three flexure specimens machined from tensile rods at an applied stress of 350 MPa. All three specimens survived in excess of 200 hours prior to termination of the testing.

BASELINE PRESSURE CASTING VERIFICATION - ITERATION N

A set of NSF tensile rods were cast using a repeat batch of baseline C-series slip to validate the baseline mechanical properties data. A total of 18 NSF tensile bars were cast for this third iteration (designated Iteration N) and tested for room temperature fast fracture strength. There was a high incidence of buttonhead failures (11 of 18) which fractography established to be due to machining damage at the buttonhead radius (BHR). These were machined prior to revision of the BHR surface finish specification which is discussed below. The 7 successful gage length fractures demonstrated exceptionally high strength levels ranging from 818-1056 MPa with a mean strength of 923 MPa and Weibull Modulus of 13; an improvement over the baseline C-series results above. On the basis of published data⁵ for commercially available structural Si₃N₄ materials (e.g. PY6, GN-10 and NT154) which indicated state-of-the-art RT average tensile strength at the 720 MPa level, the data for this pressure cast material represented a significant technical advance.

Fractographic evaluation established that 6 of the 7 specimens failed from machining related defects. Three of these six failed from the effects of machining damage in combination with a surface pore or agglomerate, Figure 4-5. One specimen failed from a surface scratch normal to the longitudinal axis, Figure 4-6. This damage may have been inflicted during the rough grinding operation. There was one volume failure due to a 30 µm agglomerate in the gage section.

Two elevated temperature (1370°C) fast fracture tests were conducted in this iteration. In one case failure originated from one of the numerous (2-20 µm surface length) machining pullouts that marred the surface of this specimen, Figure 4-7. The second 1370°C test was conducted on a specimen without noticeable machining defects. Its failure origin was not evident from fractographic evaluation. The 1370°C strength levels were 395 and 397 MPa.

Two 1230°C stress rupture tests were conducted. The first test was loaded to an applied stress level of 250 MPa. It failed after 2 hours and the origin was traced to a surface machining groove and subsequent slow crack growth, Figure 4-8. The second test was run at a reduced stress of 200 MPa but survived only 0.8 hours due to failure from a 165 µm Fe/Y rich volume inclusion, Figure 4-9.

Figure 4-5: Failure Origin of Specimen ($\sigma_f=898$ MPa) Showing Machining Marks and Agglomerate at the Surface.

Figure 4-6: Failure Origin of Specimen ($\sigma_f=879$ MPa) Showing a Severe Circumferential Scratch.

Figure 4-7: Machined Surface and Failure Origin of Specimen Fractured at 1370°C ($\sigma_f=395$ MPa) Showing 2 - 20 μm Machining Pullouts.

MACHINING ISSUES

The final cylindrical buttonhead tensile specimens were machined to the ORNL design with a gage diameter of 6.0 ± 0.1 mm. All specimens for the main body of strength data were machined using a specifically designed SOP developed for this geometry. It should be noted that the gage section was longitudinally ground during both the roughing and finishing steps.

Two comprehensive studies were pursued to establish optimum machining practice. The first involved a machine shop qualification which established specifications for control of the buttonhead failure issue. The second involved specs for control of machining damage in the gage length as it influences tensile strength of NSF bars.

Figure 4-8: Failure Origin of Specimen Fractured at 1230°C During Stress Rupture Showing a Machining Mark and Slow Crack Growth.

Figure 4-9: Failure Origin of Specimen Fractured at 1230°C During Stress Rupture Showing an Iron/Yttrium Rich Inclusion.

Machining Related Buttonhead Failure

A significant number of buttonhead failures persisted for Stage II specimens even after resolution of the forming issues that caused critical flaws in the buttonhead radius region. Profilometry measurements were taken at the BHR of a large number of specimens of Iterations 3 and 4 (N and O) to establish whether poor surface finish was the source of the problem. The results clearly show that surface finish was the major cause of the problem.

An experiment was devised to establish how machining practice influences tensile bar strength. Three machine shops were chosen to participate in the study with each employing its proprietary procedure (type diamond wheel, fixturing, method of BHR grinding, etc.) to meet a surface finish specification (R_a) at the gage and BHR of $0.41 \mu\text{m}$. The three shops involved in the study routinely met and exceeded this requirement in the gage length, with R_a values in the $.13-.18 \mu\text{m}$ range. The finish of the BHR varied significantly both above and below the specification and this provided the basis for correlating buttonhead failure to finish.

The overall average BHR surface finish of NSF specimens which failed at the BHR was found to be $0.51 \mu\text{m}$. The average for non-BHR failure was $0.38 \mu\text{m}$. Table 4-6 gives the average R_a measured at the BHR of specimens machined at the three shops, designated as shops A, B and C. Also listed are the percentages of specimens from each shop which failed at the BHR. Shop A finished to an average R_a of $0.49 \mu\text{m}$ with a resulting 51% BHR failures. Shop C supplied bars with an average R_a equal to $0.25 \mu\text{m}$ and this resulted in only 4% BHR failures (1 of 24). The R_a results from shop B averaged $0.33 \mu\text{m}$, within specification, but nonetheless 33% of the specimens failed at the BHR. The data clearly show that a more stringent surface finish specification was required in the buttonhead region for the high strength materials being processed in this program.

Table 4-6: Buttonhead Radius Surface Finish - Failure Data

Machine Shop	Average R_a μm	Buttonhead Failures %	n
A	.49 +/- .06	51	38
B	.33 +/- .08	33	18
C	.25 +/- .06	4	24

As a result of this study, the R_a spec was reduced from $0.41 \mu\text{m}$ ($16 \mu\text{in}$) to $0.25 \mu\text{m}$ ($10 \mu\text{in}$) at the buttonhead radius and to $0.2 \mu\text{m}$ ($8 \mu\text{in}$) along the gage length.

The machining requalification study described above was conducted in part with specimens from Iteration O. Nineteen (19) of 32 room

temperature NSF fast fracture tests were successful gage section failures and resulting strength values ranged from 586 to 950 MPa and averaged 789 MPa, with a characteristic strength of 839 MPa and Weibull Modulus of 8.5. In spite of excellent surface finish ($R_a = .13-.18 \mu\text{m}$), SEM fractography suggested that the majority of these gage failures initiated from machining defects, ranging from 5 μm wide axial grinding marks to >750 μm transverse scratches, Figure 4-10 a,b,c. Associated with the axial grind marks are subsurface thumbnail shaped cracks. Fracture mechanics was employed to provide critical flaw size predictions as a guide to interpretation of the SEM fractography as is discussed below. A small percentage of the failure origins involved inclusions ranging in size from 20 to 135 μm , Figure 4-11.

The surface finish comparisons conducted in the machining study indicated no statistically significant surface finish difference in the gage length region of specimens machined by shops A, B and C. Nonetheless, the strength data for a subset of 8 bars which was machined by shop C was so outstanding ($\sigma_o=904 \text{ MPa}$, $m=28$) that the machining method employed by shop C (roughing as well as finish grinding) was incorporated as SOP in further iterations.

Fractography - Strength Correlation

A limited amount of fractography data was analyzed to establish quantitative relationship between strength and flaw size. Strength data for specimens which failed from machining damage related surface flaw failures are plotted as a function of $1/\sqrt{a}$ in Figure 4-12. The maximum depth of the surface flaw (not the surface length) is plotted as the dimension a . There is excellent agreement between the regression line and the semi-circular surface crack fracture mechanics prediction⁶:

$$\sigma_t = 0.71 K_{Ic}/\sqrt{a} \quad (4-1)$$

This prediction was developed using the iteration average K_{Ic} value of 5.35 $\text{MPa}\sqrt{\text{m}}$. This correlation supports the view that strength impairing machining defects take the form of distinct surface flaws beneath individual grinding grooves. The prediction following from the long surface crack model⁷ (0.71 replaced by 0.50 in equation (4-1)) can be seen to fall significantly below the test data.

Gage Length Machining Optimization

Four distinct machining procedures (including the original SOP) were evaluated for their influence on tensile strength as an additional experiment. The four machining procedures differed according to intermediate grinding steps, diamond wheel grit size and depths of cut as outlined in Table 4-7. This experiment maintained the R_a specs while altering the rough and intermediate grinding steps with the goal of reducing subsurface damage due to the prior step. On the basis of the grinding parameters employed, the machining procedures were ranked according to operational precision from #1 to #4, with #4 being the most precise procedure. Consistent with the focus on machining damage

effects, the specimens were not given post-machining heat treatments for the purpose of this study. A total of 72 specimens from 3 HIP runs were machined and tested for this study. The procedures were rated by statistical analyses of tensile strength data.

To properly evaluate the differences between the four procedures, only those specimens that failed from surface originating flaws were considered (64 of 72). An ANOVA test was performed to compare differences in the data. Of the four machining procedures, the procedure #1 (original SOP) had the least variability, Table 4-8. In spite of the major differences in operational precision, there was no statistically significant effect of procedure on strength as shown in Table 4-8. R_y (maximum peak to valley) surface finish values were found to differ for #1 & #2 vs. #3 & #4 and are also shown in Table 4-8. Since the primary consideration was assuring a high reliability, the procedure with the least variability (#1) was chosen for future machining and can be used as a benchmark for further machining experiments.

Figure 4-10a: Failure Origin ($\sigma_f=596$ MPa) Showing a Severe Radial Grinding Mark.

Figure 4-10b: Failure Origin ($\sigma_f=899$ MPa) Showing a 5 μm Wide Machining Mark.

Figure 4-10c: Failure Origin ($\sigma_f=899$ MPa) Showing a 5 μm Wide Machining Groove and Sub-surface Thumbnail Shaped Flaw

Figure 4-11: Failure Origin ($\sigma_f=787$ MPa) Showing an Inclusion Containing Fe, Cr, Ni.

Machining Damage Failure Origins Pressure Casting - Iteration O

Figure 4-12: Strength-flaw Size Correlation for Machining Damage Failure Origins.

Table 4-7: Procedure Steps for Machining Tensile Rods.

Procedure	Roughing Step	Intermediate Step(s)	Finishing Step
#1 Original SOP	180 grit	-	320 grit (0.51mm)*
#2 Experimental	320 grit	320 grit	320 grit
#3 Experimental	180 grit	320 grit	800 grit (0.15mm)
#4 Experimental	180 grit	320, 400, 600 grit - (0.05mm) (0.05mm)	800 grit (0.05mm)

*(0.51mm) refers to amount of stock removed by that step.

Table 4-8: Machining Procedure Strength Data.

Procedure	Mean Strength (MPa)	Standard* Error (MPa)	Surface Finish R_a (microns)	Number of Specimens n
1 (SOP)	812	18	1.26	31
2 (Experimental)	767	35	1.33	10
3 (Experimental)	847	30	0.77	14
4 (Experimental)	845	42	0.68	9

* standard error = standard deviation/ $\sqrt{n}$

TENSILE DATA FOR PROCESS OPTIMIZATION

The Stage II experimental plan involved 16 processed batches of silicon nitride and each of the experimental blocks was evaluated through room temperature tensile tests using approximately thirty tensile rods amounting to a total of over 500 rods tested. These data are summarized in Figure 4-13. The doublets for Iteration V and Z are from the oxidation treatment experiments while for Iteration O the 3 values correspond to the 3 machining procedures employed.

Figure 4-13: Mean Tensile Strengths From Stage II Iterations

The unit operation control variables evaluated in the experimental plan were:

- * Binder. (2)
- * Surfactant. (2)
- * Casting rate. (2)
- * Solids loading. (2)
- * Pre-HIP treatment. (2)
- * HIP cycle. (2)
- * Fixturing. (2)

The results of the experimental plan defined the set of optimum process conditions used in the Stage III process demonstration.

Critical Flaw Population Shifts

By the nature of the experimental plan, there were significant differences from iteration to iteration in the tensile strength levels corresponding to the response surface, Figure 4-13. Iterations XXX, X, Y and Z were conducted at a time when wear of processing equipment was recognized (NDE, fractography) as a significant source of contamination. The compilation of strength and fractography data for these iterations provide a valuable database on shifts in critical flaw populations. The shifts resulted from corrective actions which eliminated wear related iron contamination midway through the period.

Table 4-9 gives the strength statistics for the four sets of tensile rods which totaled 135 samples. As each subsequent batch was "cleaned up" by elimination of iron contaminating sources the mean strength increased by over 170 MPa. Optical and SEM fractography were performed on all 135 specimens and the results are summarized in Table

4-10. There was a significant shift from volume failures to surface failures with the elimination of iron contamination from Iteration XXX up to Iteration Z. The surface flaw type "Am", amorphous region, was found to be related to the post-machining heat treatment. The other significant flaw type "Mp", zone of microporosity, occurs in the volume and may be related to the densification process. It is apparent from Iteration Z data that surface flaws related to machining are the major strength and reliability limiting defects.

Table 4-9: RT Tensile Strength Data for Batches XXX - Z

Batch	Mean Strength (MPa)	Std. Dev. (MPa)	Characteristic Strength (MPa)	Weibull Modulus m	No. of Specimens
XXX	707	88	746	9.0	25
X	771	105	816	8.5	18
Y	847	103	892	9.4	45
Z	878	108	924	9.4	47

Table 4-10: Fractography Summary for Batches XXX - Z

Batch	Location		Flaw Type (%)					Size Range (μm)
	% V	% S	I	Mp	M	Am	U	
XXX	68	32	72	0	20	0	8	>100
X	29	71	41	6	24	12	17	15-50
Y	2	98	0	2	28	68	2	10-80
Z	29	71	0	40	45	9	6	5-65

V = volume
S = surface

I = iron inclusions
Mp = microporosity
M = machining damage
Am = amorphous region
U = unknown

Optimized Process Tensile Data

Near the conclusion of Stage II, a total of 53 tensile specimens were fabricated by the "optimized process". This set was found to have a mean strength of 888 MPa and a range from 548 to 1091 MPa. The corresponding tensile strength distribution is plotted in Figure 4-14. Competing risk Weibull distributions were generated for surface and volume flaw types and are shown in Figure 4-15. The Weibull moduli are

9.3 and 9.9 for surface and volume flaws, respectively. It is interesting to note that at any given applied stress level the probability of failure is higher for a surface flaw than for a volume flaw according to this data.

Figure 4-14: Weibull Plot Assuming an Unimodal Strength Distribution.

The surface flaw strength distribution in Figure 4-15 visually suggests 3 regimes within the distribution. Detailed fractography observed that within the surface flaw population there were indeed 3 flaw origin types: surface amorphous regions and two types of machining damage. The volume flaws are of one type and are characterized as agglomerate-porous zones. Figures 4-16a,b,c,d show micrographs of these flaw types. Included are atypical machining damage, normal machining damage, Si-rich amorphous regions and zones of microporosity.

Based on the fractographic data, another competing risk Weibull analysis was performed, distinguishing the 3 surface flaw and the 1 volume flaw populations. For clarity, only the three surface flaw distributions are shown in Figure 4-17. Since the strength distribution data (mean = 889 MPa and $m = 9.9$) from the volume failures are from only one flaw type, the modulus does not change. However, the three distributions from the surface flaw data show very different results.

Figure 4-15: Weibull Plot Using Competing Risk for Surface and Volume Failure

Figure 4-16a: Failure Origin ($\sigma_f = 685$ MPa) Showing Atypical Machining Damage

Figure 4-16b: Failure Origin ($\sigma_f = 921$ MPa) Showing an Amorphous Region

Figure 4-16c: Failure Origin ($\sigma_f = 944$ MPa) Showing Normal Machining Damage

Figure 4-16d: Failure Origin (of = 1040 MPa) Showing a Volume Defect Containing Microvoids.

Figure 4-17: Competing Risk Weibull Plot for Three Surface Flaw Types.

As expected, the lowest strength and Weibull Modulus (mean = 696 MPa and $m = 6.4$) were from specimens having atypical machining damage as the critical flaw origin. The middle strength values (mean = 867 MPa and $m = 11.6$) are from Si-rich amorphous origins. These defects developed during the annealing process and their precursors may be from local inhomogeneities in the microstructure or from subsurface cracks formed during machining. These strengths overlap both the atypical machining damage and normal machining damage. The third and highest mean strength and Weibull Modulus (954 MPa and 15.2) are from specimens that had surface flaws from normal machining (procedure #1).

EFFECTS OF HEAT TREATMENT ON TENSILE STRENGTH

Iteration V specimens were used to evaluate the effects of post-HIP and post-machining heat treatments on room and elevated temperature tensile strength. The post-HIP treatment is conducted prior to machining to crystallize the secondary phases present after densification. The post-machining treatment is performed to anneal and oxidize (blunt) surface and near surface flaws caused by the grinding process. A total of 63 room temperature and 13 elevated temperature (1370°C) tensile tests were conducted on specimens which comprised the 2x2 experimental matrix.

The mean values of tensile strength for the four categories of room temperature tests are plotted in Figure 4-18. It is apparent that in general, crystallization (XTAL) can decrease the RT strength although the data suggest the effect is statistically insignificant, while oxidation (OXID) increases it. ANOVA data analysis suggests a 1% XTAL mean strength decrease and an 11% OXID increase. The individual mean strength values were 743, 719, 806 and 811 MPa for the four conditions (NONE, XTAL, OXID, BOTH) plotted in Figure 4-18.

While the oxidation treatment appears to have a significant effect on the character of the surface flaw population, apparently crystallization does not influence the room temperature strength limiting volume defects. There is a small interaction of the two treatments which is also displayed in Figure 4-18.

Figure 4-18: Mean Room Temperature Tensile Strength as a Function of Heat Treatment Condition.

Iteration Z specimens were subsequently used to validate the oxidation strength enhancement observed in Iteration V. Fifteen (15) specimens were tested in the as-machined condition. These had a mean RT strength of 834 MPa. Thirty-two (32) specimens were given a post-machining heat treatment and were tested for RT fast fracture strength. The resultant mean tensile strength for these 32 specimens was 891 MPa. This represented a 7% strength enhancement by the oxidation treatment which is consistent with the Iteration V experimental results.

The 1370°C mean tensile strength data are summarized in Figure 4-19. Without either treatment (NONE), the mean was 347 MPa while with both, the mean was 480 MPa, a significant increase of 38%. The interaction effect is evident in Figure 4-19. ANOVA suggests that an 18% increase is attributable to crystallization and a 16% increase is attributable to oxidation alone.

Figure 4-19: Mean 1370°C Tensile Strength as a Function of Heat Treatment Condition.

RESIDUAL STRESS IN NSF BARS

An assessment of near surface, machining induced residual stress states in NSF tensile bars was conducted at the Army Material Technology Laboratory. The x-ray diffraction approach with Cu K_α radiation was used. The $\sin^2 \psi$ stress measurement technique was employed to provide quantitative data on a total of 13 NSF bars. A number of MOR bars and a Si_3N_4 powder sample were evaluated in the course of the developmental work. This technique provides a stress measurement which represents a bulk volume average, as opposed to point values. In this study, 50% of the diffracted volume is within 22.8 μm of the specimen surface.

The stresses in the gage section were the primary focus of this work. Longitudinal stresses measured at the center of the gage length were invariably found to be compressive, with magnitudes ranging from 200 to 400 MPa. Hoop stresses when detectable were found to be tensile with magnitude ranging to 70 MPa.

The technique was utilized to establish the dependence of residual

stress on post-machining heat treatments, grinding methods of different machine shops and forming (injection molding vs. pressure casting) methods. No effect was found on the as-machined stress state after a series of trial heat treatments. Likewise, no significant differences in residual stress were found in the assessment of specimens machined at three machine shops. A difference was found when comparing injection molded and pressure cast final machined specimens. The cast specimens were found to have a higher level of compressive stress than the injection molded specimens, 350 MPa vs. 245 MPa. This could be a result of the green density gradients inherent to the casting process, which cause HIP related residual stresses.

In an attempt to measure HIP related residual stresses, one specimen (R-16) was partially machined in the gage section. Residual stress analysis was performed at 8 orientations corresponding to four different depths of machining as well as the as-HIP'ed surface (0° orientation). No significant difference in residual stress was found after grinding to depths of 0.012, 0.048, 0.104 and 0.114 inches.

An unexpected result in this study involved the x-ray diffraction integrated intensity which was found to increase with depth of machining, Figure 4-20. This integrated intensity is proportional to the % β -phase Si_3N_4 . As such, the data form a trace of the diminishing α -phase of the HIP reaction layer. This result suggests a potentially useful Q.C. method for assessment of reaction layer removal in machining.

MONITORING OF BENDING IN TENSILE TESTING

Several specimens were strain gaged prior to testing, to study bending during testing and to determine what, if any, effect bending has on strength and reliability data. Each specimen had four gages mounted around the center of the gage section and located every 90°. The amount of bending is calculated in accordance with ASTM Test Method for Sharp-Notch Tension Testing with Cylindrical Specimens (E 602) in the following manner:

(4-2)

$$\% \text{ Bending} = \frac{2 [(g_1 - g_3)^2 + (g_2 - g_4)^2]^{1/2}}{(g_1 + g_2 + g_3 + g_4)} \times 100$$

where

g_1 , g_2 , g_3 and g_4 are the strain gage readings in units of strain.

A Daytronic System 10 DataPAC was used to monitor and record the strain and load data. Initially, 25 tensile specimens were strain gaged and the load-bend data were recorded without any realignment. The measured bending at failure was < 5.5% for 24 of the 25 specimens while one was at 12.5%. This assured proper alignment of the test fixtures and the validity of the data.

As part of the experiment 50% (predetermined randomly) of a group of 30 specimens were to be realigned if the measured bending at a preload of 6668 N (1500 lbs.) was > 10%. The realignment involves unloading the specimen, twisting the grip/collet load train assembly and reloading the specimen. If the measured bending was still greater than

preload of 6668 N (1500 lbs.) was $> 10\%$. The realignment involves unloading the specimen, twisting the grip/collet load train assembly and reloading the specimen. If the measured bending was still greater than 10% , the realignment was performed a second time and the specimen was tested to failure regardless of the measured preload bending. Load-displacement curves have a "knee" in the curve at about 5556 N (1250 lbs.) where the copper collets deform into the buttonhead radius. Therefore the preload was chosen to be higher than 5556 N to monitor the "preload" bending.

Figure 4-20: X-ray Diffraction Residual Stress Results

Figure 4-21 shows representative load-bend curves for strain-gaged specimens. A typical curve shows an increase in bending during initial loading but as the collets seat themselves the bending begins to decrease. The Figure shows that the range of bending at the preload level (6668 N) is 4 to 16% , and in all cases the bending at failure is $\leq 6\%$. For two of the specimens for which realignment took place, the best bending achieved at the preload was 12% , but still resulted in low (2%) bending at failure. However, as shown in Figure 4-22, and consistent with the decreasing bending level after preload, there appears to be a trend that the higher strength specimens experience a lower bending at failure. Also noteworthy is that the specimens that had a realignment performed have a lower $\%$ bending at failure than those without a realignment.

specimen. Two Weibull Moduli were calculated. The first modulus was determined from the standard fracture stress of each specimen (load/area) and was equal to 10.04. A second or predicted fracture stress was determined as the product of the maximum strain times Young's Modulus (310 GPa). A Weibull analysis was performed using the predicted strengths giving a value of 10.27. For practical purposes the difference is negligible. It was therefore concluded that 100% strain gaging is not required. However, a periodic sampling using a strain gaged specimen to check load train alignment was conducted.

Figure 4-21: Typical Load vs. Bending Curves for Strain Gaged Tensile Specimens

Figure 4-22: Bending at Failure vs. Tensile Strength

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APPENDIX 5: TENSILE STRENGTH - FRACTOGRAPHY DATABASE

Table 5-1: NCX-5102 Database Summary

Failure Origin	Average (MPa)	Std. Dev (MPa)	Count
All	997	115	320
By Location			
Surface (S)	1001	107	247
Volume (V)	984	138	73
By Type			
Extrinsic	984	133	150
Machining (M)	999	122	134
Inclusion (I)	865	162	16
Intrinsic	1008	96	170
Amorphous (Am)	1005	88	107
Microporosity (Mp)	1021	106	55
Unknown (U)	960	118	8

Figure 5-1: Tensile Strength Data by Flaw Type

Table 5-2: NCX-5102 Database

Rank	Rod #	Tensile Strength (MPa)	Flaw Location	Flaw Type
1	L-169	540	S	M
2	L-91	578	V	I
3	J-121	606	V	I
4	M-137	619	V	I
5	L-97	679	S	M
6	M-158	706	S	M
7	M-159	740	V	U
8	L-168	753	S	M
9	M-138	779	V	I
10	L-170	786	V	Mp
11	J-21	809	V	I
12	H-25	812	S	M
13	I-125	813	V	Mp
14	L-37	816	S	M
15	H-6	822	S	Am
16	I-132	822	S	M
17	M-75	826	S	M
18	H-163	834	S	Am
19	I-10	834	S	Am
20	H-108	835	V	I
21	I-68	836	V	Mp
22	I-144	837	S	M
23	L-59	839	S	Am
24	H-89	843	V	Mp
25	H-99	847	S	M
26	M-56	853	V	Mp
27	M-55	855	V	Mp
28	H-97	856	V	I
29	L-117	857	S	M
30	I-18	859	S	M
31	M-155	860	S	M
32	L-83	861	S	Am
33	I-21	862	S	Am
34	I-82	862	V	I
35	I-123	862	S	M
36	M-3	863	S	M
37	L-35	865	S	M
38	J-81	866	V	I
39	J-45	866	S	M
40	I-94	868	S	M
41	J-89	870	S	Am
42	I-22	871	S	M
43	M-16	871	S	M
44	I-17	871	S	M
45	M-82	874	S	M

46	I-23	875	S	M
47	I-72	877	V	Mp
48	M-76	878	S	Am
49	J-71	878	S	M
50	I-7	879	S	M
51	M-69	882	S	M
52	M-91	883	S	Am
53	L-100	883	S	Am
54	I-15	884	S	M
55	L-180	886	S	Am
56	L-15	889	S	Am
57	M-67	893	S	Am
58	I-156	893	S	Am
59	M-11	893	S	M
60	M-86	894	S	M
61	L-84	897	S	M
62	L-32	898	S	M
63	L-52	899	S	M
64	H-8	900	V	Fe
65	H-40	901	S	Am
66	L-104	903	S	M
67	I-97	904	S	I
68	I-26	905	S	Am
69	I-38	905	S	M
70	M-33	906	V	Mp
71	M-141	907	S	M
72	L-94	908	V	Mp
73	M-68	917	S	M
74	J-47	918	V	Mp
75	M-57	919	S	M
76	M-144	920	S	M
77	L-4	920	S	M
78	J-107	921	S	Am
79	M-112	921	S	Am
80	L-85	923	S	Am
81	H-152	924	S	Am
82	H-21	924	S	Am
83	M-18	925	S	M
84	M-153	925	S	U
85	M-27	927	S	M
86	H-42	927	S	Am
87	L-74	927	S	Am
88	K-77	930	V	Mp
89	L-173	931	V	I
90	L-136	931	V	Mp
91	H-105	931	S	Am
92	L-108	936	S	Am
93	M-140	936	S	Am
94	L-17	936	S	M
95	J-27	938	V	Y
96	M-90	939	S	M
97	M-96	941	S	Am

98	H-7	941	S	Am
99	J-120	943	S	Am
100	M-29	944	S	M
101	M-54	945	S	Am
102	M-39	945	S	M
103	H-13	945	S	M
104	J-108	946	S	Am
105	I-35	947	S	Am
106	M-92	948	S	Am
107	M-147	948	S	M
108	I-24	949	S	Am
109	L-47	949	V	Mp
110	M-6	949	V	Mp
111	M-22	951	S	M
112	M-53	952	S	Am
113	J-106	952	S	Am
114	J-59	954	S	Am
115	J-169	954	V	Mp
116	L-56	955	V	Mp
117	J-153	955	S	M
118	M-38	959	S	M
119	J-115	960	V	Mp
120	L-105	961	V	Mp
121	L-120	961	S	M
122	I-143	962	S	M
123	M-44	964	S	M
124	H-141	966	S	M
125	I-83	966	S	Am
126	L-16	968	S	Am
127	J-105	970	V	Mp
128	J-48	971	S	M
129	H-109	972	S	M
130	I-122	973	S	Am
131	M-71	973	S	M
132	I-88	973	S	M
133	J-20	974	V	I
134	M-152	974	S	U
135	J-54	975	S	M
136	I-131	976	S	Am
137	L-3	978	S	M
138	I-89	978	S	Am
139	L-179	979	S	M
140	M-134	979	V	I
141	H-136	982	V	Mp
142	J-109	984	S	Am
143	H-140	984	S	M
144	M-94	985	S	M
145	L-33	985	S	Am
146	J-63	986	S	Am
147	M-85	986	S	Am
148	H-52	987	S	Am
149	H-23	987	S	Am

150	L-114	988	S	M
151	M-45	988	S	M
152	L-54	988	V	Mp
153	H-151	989	S	Am
154	K-94	989	S	Am
155	J-41	991	S	M
156	M-64	991	S	M
157	I-139	995	S	Am
158	L-122	996	S	Am
159	J-83	996	S	Mp
160	M-21	996	S	M
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167	I-60	1002	S	U
168	M-70	1003	S	M
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171	H-15	1007	S	Am
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317	L-13	1217	S	Am
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