ADDITIVE EFFECTS ON THE HYDROTHERMAL DEGRADATION OF HOT-PRESSED SILICON NITRIDE SPHERICAL ROLLING ELEMENTS

By

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This document is dedicated to my family for their unwavering guidance and support.
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By

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Chair: Darryl P. Butt
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The hydrothermal degradation of three bearing grade silicon nitrides was investigated. Dissolution of Si$_3$N$_4$ was observed at temperatures of 250°C, 300°C, and 325°C. Each Si$_3$N$_4$ lost weight with the kinetic process following the linear rate law. Apparent activation energies of 76 and 70 kJ/mol were calculated for Cerbec SN101C and Toshiba TSN-03NH Si$_3$N$_4$ respectively. Silicon oxynitride scales on the surface of the Si$_3$N$_4$ balls were confirmed using SEM and XPS. Test solution chemistry was analyzed by monitoring pH and by the detection of dissolved species using ICP. The proposed rate limiting mechanism is the surface-controlled hydrolysis reaction taking place at the SiO$_x$N$_y$/H$_2$O interface.
CHAPTER 1
INTRODUCTION

Silicon nitride (Si$_3$N$_4$) materials have been considered for use in aeropropulsion engines due to their low density, high strength, and thermal stability. Their proposed uses include turbine blades and hybrid bearings. It is therefore necessary to study the stability of Si$_3$N$_4$ in a variety of field conditions that include exposure to water vapor, jet fuel, and elevated temperatures and pressures. The parabolic behavior of Si$_3$N$_4$ in dry oxygen environments is well established in the literature. This project will investigate, in particular, the behavior of hot pressed silicon nitride spherical rolling elements under hydrothermal conditions.

**Ball Bearing Systems**

A rolling surface encounters less friction and wear than a sliding surface. Ball bearing systems take advantage of this principal in order to minimize the friction in rotating parts by translating both thrust and torque. A ball bearing system consists of four main components: the balls (spherical rolling elements), the cage, the raceway, and the lubricant. Figure 1-1 is a schematic of a ball bearing system used in an aircraft engine. Spherical balls are placed between the inner and outer raceways and are held in place by the cage. Lubrication in the form of oil or grease is applied to the system as a means to further reduce wear and friction. It is imperative that the rolling elements possess a highly polished surface. Surface asperities interfere with the rolling process and lead to increased wear. They can also serve as corrosion initiation sites.
The balls are subject to both radial and thrust loads which are transmitted from the ball to the inner raceway and from the outer raceway to the ball. The magnitude of the loads that each ball can bear is limited due to the small contact area that is created between each ball and each raceway. This contact area is also referred to as the Hertzian contact zone and is illustrated in Figure 1-2. Due to this small contact area, any debris that may lodge itself between a ball and a raceway will act as a stress concentrator and potentially cause the bearing to fail.

For the case of aircraft engines, where operation occurs at high temperatures and high revolutions per minute (rpm’s) for extended periods of time, the bearing systems are critical. Any malfunction of the bearing system can lead to catastrophic failure and possibly a loss of human life. Current bearing system designs utilize stainless steel components (particularly M50, AISI 52100, and/or AISA 440C) to reduce friction in the engine’s main shaft. These systems, however, are subject to encounter many problems in
addition to the fragility already associated with the design of the ball bearing system itself. For example, electron transfer between the metal components can lead to corrosion. The resulting pits that form on the surfaces of the bearing constituents can lead to failure as their surface roughness is increased. Corrosion products can also cause damage to the system as discussed above in the case of debris entering the system. Lubricant chemistry may also be altered if a reaction occurs with the corrosion products. Another problem includes the possible welding between metal components when they are exposed to high temperatures and pressures without proper lubrication.

Figure 1-2. Hertzian contact zone resulting from the rolling between the surfaces of bodies a and b (Johnson, 1985).
Hybrid Ball Bearing Systems

The complications associated with the traditional stainless steel bearings can be alleviated by incorporating ceramic rolling elements. Hybrid ball bearing systems utilize ceramic balls while the cage and the raceways remain stainless steel. Material candidates for the rolling elements must meet the aforementioned requirements for stability in an aircraft engine environment. Ideal candidates possess a low thermal expansion coefficient and are both lightweight and stiff. For example, lightweight components reduce the weight of the aircraft engine, thus making it faster and more efficient. Low thermal expansion materials are not susceptible to the rapid temperature changes observed in an aircraft engine. The overall structural integrity of the engine is maintained using stiff and mechanically sound components. Titanium carbide (TiC), titanium carbonitride (TiCN), and silicon nitride are an example of such candidates.

One advantage of a hybrid bearing is that electron transfer is eliminated when a non-conducting ceramic compound such as Si$_3$N$_4$ is used. Possible welding between the ceramic balls and the steel raceways is also prevented. Because Si$_3$N$_4$ is stiffer than the stainless steel used in current rolling elements, the Hertzian contact zone is reduced. Therefore, less material will be in contact with the raceways at any given time, and the life of the bearing will increase.

Research Objective

The aforementioned benefits of hybrid bearings have yet to be realized in either military or commercial aircraft engines. A great deal of stability testing is still needed. Any component that is to be incorporated into an aircraft engine must be able to sustain harsh environmental conditions, such as water vapor.
Previous studies have shown differences between the oxidation of bearing grade Si₃N₄ and CVD Si₃N₄. Bearing grade Si₃N₄ stability in hydrothermal conditions, however, has not been studied in great detail with regards to the effects of different types of sintering additives. This project was designed to compare the oxidation behavior of three different types of Si₃N₄ spherical rolling elements (each with a unique combination of additives) exposed to water vapor. In addition to the kinetic analysis already found in the literature, the microstructure of the Si₃N₄ balls and the water chemistry of the test solutions will be analyzed.
CHAPTER 2
LITERATURE SURVEY

This chapter provides a summary of the scientific literature that was compiled in order to gain a greater understanding of the relationship between silicon nitride and the mechanisms behind its oxidation in hydrothermal conditions.

**Si₃N₄ Structure and Properties**

The need for materials that are resistant to high temperatures and corrosion continues to rise as the demands for faster, more efficient engines in both military and commercial aircraft increases. In the design of the ball bearing system, in particular, materials with a high degree of wear resistance are also required. Silicon nitride is an ideal candidate for engine and bearing applications due to its superior resistance to both thermal shock and mechanical wear compared to stainless steel.

The basic tetrahedral structure of silicon nitride is shown in Figure 2-1. The bulk structure of Si₃N₄ consists of these tetrahedral units with shared corners. Although this structure is also found in silica, the stronger silicon-nitrogen bonds account for silicon nitride’s rigidity. Since nitrogen prefers to form three bonds, rather than two for the case of oxygen, Si₃N₄ does not possess the flexible bridge bonds that are found in silica (SiO₂). The Si and N atoms are 4-fold and 3-fold coordinated, respectively. With respect to planar geometry, three silicon atoms are arranged in an equilateral triangle around a single nitrogen atom, thus forming bond angles of 120º. The bonding is similar to an sp² bond consisting of three hybrids of s, px, and py orbitals, while the pz orbital is non-bonding and out of the plane.
Figure 2-1. Tetrahedral structure of Si$_3$N$_4$ (Dobkin, 2003).

Silicon nitride can be either crystalline or amorphous. Silicon nitride produced by chemical vapor deposition, or CVD Si$_3$N$_4$, is typically amorphous due to the rapid cooling of the Si and N atoms onto the substrate. Bearing grade Si$_3$N$_4$, discussed in detail later in this chapter, is polycrystalline. In either case, the dense structure of Si$_3$N$_4$ restricts even the smaller positive ions (i.e., H$^+$, Na$^+$, or K$^+$) from diffusing through the lattice. Nitrides, for example, are even used as etch stop layers for both plasma etching and wet etching since they do not possess the typically more open structures of oxide ceramics. This is why ion diffusion occurs along the grain boundaries in polycrystalline Si$_3$N$_4$ which is the focus of this project.

**Si$_3$N$_4$ Polymorphs**

The two most common polymorphs of silicon nitride are $\alpha$-silicon nitride and $\beta$-silicon nitride. Each polymorph possesses unique structures, properties, and regions of stability. This section highlights the differences between the two polymorphs of Si$_3$N$_4$ that are used to produce bearing grade Si$_3$N$_4$. 
**α-Si$_3$N$_4$**

The hexagonal structure of α-Si$_3$N$_4$ is shown in Figure 2-2. Beta-Si$_3$N$_4$ possesses the same hexagonal structure, but is actually a mirror image of the α-Si$_3$N$_4$ structure pictured in Figure 2-2. Since there is no rotational symmetry between the two structures, the alpha-to-beta phase transformation can only occur via the termination of the high-strength silicon-nitrogen bond. This transformation occurs in liquid phase sintering which will be discussed later in the chapter.

![Figure 2-2. The hexagonal crystal structure of α-Si$_3$N$_4$ (Dr. Stephan Rudolph).](image)

**β-Si$_3$N$_4$**

In β-Si$_3$N$_4$, the strength value of the silicon-nitrogen covalent bond is one of the highest found in nature. Although α-Si$_3$N$_4$ is harder than β-Si$_3$N$_4$, it is slightly less stable. Its microstructure consists of needle-like β-Si$_3$N$_4$ crystals with the hexagonally close packed (HCP) atomic arrangement. These crystals are essential to the optimization of Si$_3$N$_4$. Experiments have shown that the toughness of β-Si$_3$N$_4$ decreases with creep resistance (Wiederhorn et al., 1999). Therefore, the trade-off for the microstructural optimization of Si$_3$N$_4$ that is to be exposed to high temperatures is a decrease in its
toughness. Microstructures continue to be optimized at present in hybrid bearings, where both toughness and creep resistance are necessary.

**Bearing Grade Si$_3$N$_4$**

The latest form of Si$_3$N$_4$ is created through a novel process developed at the University of Pennsylvania. This process involves exposing $\beta$-Si$_3$N$_4$ that is mixed in with sintering additives to high temperatures (typically around 1800ºC) and nitrogen pressures of 10-100 atm. The crystals formed are also needle-like, and, therefore, the material has an increased toughness that is now on the order of that of silicon carbide (SiC). Silicon nitride materials that are synthesized in this manner are now being considered for gas turbine applications.

The Si$_3$N$_4$ balls themselves are manufactured through hot isostatic pressing (HIPing). Silicon nitride powders are combined with binders and sintering aids to form a slurry. The slurry is spray dried to yield a free-flowing powder that can be pressed into green balls, or ball blanks. Then, the binders are removed from the ball blanks via air firing. Next, the blank is loaded into a graphite crucible with encapsulated glass where it is finally densified at a high temperature and pressure resulting in a ball with almost zero degree of porosity. Once the ball is hot-pressed, the surface is finished via a diamond lapping process.

Prior to HIPING, metal oxides such as magnesium oxide (MgO) and alumina (Al$_2$O$_3$) are added to densify the Si$_3$N$_4$ during sintering. Most bearing grade Si$_3$N$_4$ contains less than 15 wt.% sintering aids. These sintering aides, however, are responsible for the formation of residual intergranular and crystalline phases that have been found to deteriorate the mechanical properties of the ball at high temperatures. During sintering, any residual SiO$_2$ on the surface of the Si$_3$N$_4$ powder reacts with the sintering aids to
form a silicate phase that surrounds each Si$_3$N$_4$ grain. These silicate grain boundary layers are generally amorphous with thicknesses ranging from 0.5 to 1 nm depending on the sintering aids used (Clarke, 1987). Another name for this process is liquid phase sintering, where the liquid, which allows for mass transport during densification, solidifies upon cooling into what most refer to as a glassy phase. More specifically, α-Si$_3$N$_4$ dissolves into the liquid, and β-Si$_3$N$_4$ precipitates out. Therefore, no true grain boundaries exist. These pseudo-grain boundaries are more susceptible to corrosion than the Si$_3$N$_4$ grains themselves. The more liquid present, the lower the temperature and pressures need to be in order to form a dense ceramic. Keep in mind that the HIPING temperature and pressure need to be sufficient enough to thermodynamically and kinetically promote the α-Si$_3$N$_4$ to β-Si$_3$N$_4$ phase transformation. Therefore, the amount of sintering aids added to the slurry need to be optimized in order to form a dense, mechanically sound, and corrosion resistant Si$_3$N$_4$ product.

**Si$_3$N$_4$ Oxidation**

Oxidation studies have been conducted on various types of Si$_3$N$_4$ but were mostly limited to either CVD Si$_3$N$_4$ or Si$_3$N$_4$ powders in dry oxygen or dry air environments. Little is presently known about the behavior of bearing grade Si$_3$N$_4$ under hydrothermal conditions or the underlying mechanisms behind its oxidation and eventual degradation. Even for CVD Si$_3$N$_4$ which has been studied extensively, the rate limiting mechanisms of oxidation are under debate. This portion of the literature review will highlight a few key studies on the oxidation of various kinds of Si$_3$N$_4$ under both dry and hydrothermal conditions.
Oxidation of Si₃N₄ in Dry Air

Oxidation studies on SiC have revealed the formation of a pure silica (SiO₂) scale on its surface. In contrast, some experiments on the oxidation of Si₃N₄ have revealed a more complicated oxide scale. In the high temperature oxidation of crystalline CVD Si₃N₄, for example, Du et al. observed the formation of a silicon oxynitride (SiNₓOᵧ) layer under the SiO₂ scale (Du et al., 1989). Since the densities of SiO₂ and SiNₓOᵧ are similar (2.2 g/cm³ and 2.69 g/cm³, respectively), thermodynamic and kinetic calculations will only slightly differ in regards to each scale (Butt et al., 1996). Therefore, Si₃N₄ oxidation in dry environments takes place by the reaction in equation 2-1.

\[
\text{Si}_3\text{N}_4 + 3\text{O}_2 \leftrightarrow 3\text{SiO}_2 + 2\text{N}_2 \quad (2-1)
\]

Parabolic weight gains due to the formation of the SiO₂ scale have been observed for isothermal exposures in dry air mixtures. Butt et al. reported similar results on the thermogravimetric analysis (TGA) of Si₃N₄ powders exposed to an ultra-high-purity N₂-20% O₂ gas environment at temperatures ranging 650º-1200ºC (Butt et al., 1996). Parabolic rate constants were reported and found to be slightly lower than those previously reported for monolithic CVD Si₃N₄. Activation energies of 400 kJ/mol were reported for temperatures above 900ºC. Below this temperature, activation energies on the order of 200 kJ/mol indicated that a different rate limiting mechanism for oxidation could have taken place. These results contradicted the theory that oxidation would be affected by the surface to volume ratio (which is very high for micron sized powders), since oxidation is a surface reaction.
Hydrothermal Oxidation of Si₃N₄

The term hydrothermal is used to refer to “hot water.” In Geology, it more specifically pertains to the rocks, ore deposits, and springs formed by natural hot water emanations on both land and on the ocean’s floor (Rona et al., 1983).

Hydrothermal experiments conducted on silicon carbide revealed that the oxidation rate increased with water vapor content (above a few volume percent water vapor). It was also determined that after the initial oxidation reaction (shown in equation 2-2 for the case of Si₃N₄), the silica layer that was formed also reacted with the water vapor by the reaction in Equation 2-3 to form a volatile species (Opila and Hann, 1997).

\[
\text{Si}_3\text{N}_4 + 6\text{H}_2\text{O} \leftrightarrow 3\text{SiO}_2 + 4\text{NH}_3 \tag{2-2}
\]

\[
\text{SiO}_2 + 2\text{H}_2\text{O} \leftrightarrow \text{H}_4\text{SiO}_4 \tag{2-3}
\]

The species formed is slightly acidic and has a limited solubility. It is this volatile H₄SiO₄ that dissolves into water by the reaction in Equation 2-4.

\[
\text{H}_4\text{SiO}_4 \leftrightarrow \text{H}_3\text{SiO}_4^- + \text{H}^+ \leftrightarrow \text{H}_2\text{SiO}_2^{2-} + 2\text{H}^+ \tag{2-4}
\]

The ammonia formed in Equation 2-1 is very soluble in water, even at room temperature. Since the dissolved species formed in Equation 2-3 is a very weak acid and is not very water-soluble, the net change in the water pH due to Si₃N₄ oxidation should be more basic.

Very little information has been provided on the underlying mechanisms of the hydrothermal degradation of bearing grade Si₃N₄. Dennis S. Fox et al., however, recently provided a very comprehensive hydrothermal study to compare bearing grade Si₃N₄ with CVD Si₃N₄ (Fox et al., 2003). Experiments were performed on three types of Si₃N₄ in a tube furnace with a 50% H₂O-50% O₂ gas mixture flowing at 4.4 cm/s. The first type of Si₃N₄ in the study was an α-Si₃N₄ produced by CVD. The AS800 samples were in situ-
reinforced $\beta$-Si$_3$N$_4$, and the SN282 samples were a $\beta$-Si$_3$N$_4$ (with a more oxidation resistant grain boundary phase) designed specifically for gas turbine environments. Weight changes were continuously measured and the oxidation kinetics determined using TGA. Paralinear kinetics was observed for the overall oxidation of Si$_3$N$_4$ in water vapor at temperatures ranging 1200-1400ºC. The formation of a silica layer is represented by an initial parabolic weight gain, followed by a linear weight loss as the silica layer volatizes.

It was found that the SN282 Si$_3$N$_4$ was more resistant to both oxidation and volitazation when compared to the CVD and AS800 forms of Si$_3$N$_4$. After approximately 50 hours of exposure, each type of Si$_3$N$_4$ began to lose weight. It has been proposed that the additives decrease the volatility of the small amount of oxide scale that is produced in addition to hindering the scale’s formation. Outward diffusion of the additive cations to the surface are also said to result in the formation of other oxides that reduce the activity of silicon in the oxide scale.

Activation energies ranging 14-338 kJ/mol were reported with a large error for the water vapor experiments conducted from 1200-1400ºC. Parabolic rate constants obtained from the water vapor experiments were 1-2 orders of magnitude higher than those found in dry oxygen. However, the proposed rate limiting mechanism is similar to that which occurs for Si$_3$N$_4$ in dry oxygen. It involves the outward diffusion of sintering aid (e.g., Y$_2$O$_3$ and MgO) cations along the Si$_3$N$_4$ grain boundaries then on into the silica layer before it volatizes. This also includes the inward diffusion of oxygen. The reported activation energies are in agreement with this proposal. For example, the lowest activation energy was associated with CVD Si$_3$N$_4$ which contains no additives. This
proposal, however, is still controversial in the field, and more hydrothermal studies on Si$_3$N$_4$ are needed to assess the underlying mechanisms of both silica scale growth and its dissolution.
CHAPTER 3
EXPERIMENTAL PROCEDURES

This chapter chronicles the experimental procedures used in the hydrothermal oxidation experiments. A description of the bearing grade Si$_3$N$_4$ samples and their preparation are provided along with a detailed description of the high temperature pressure vessel used to oxidize the samples. The chapter concludes with a brief account of the analysis of the oxidized samples.

**Si$_3$N$_4$ Samples**

Three types of silicon nitride balls were investigated. Figure 3-1 shows the as-received samples. Table 3-1 lists the elemental compositions of the additives for each type of ball in wt.%. Both the NBD200 and the SN101C balls were manufactured by Cerbec, a division of Saint-Gobain Ceramics. They have a fracture toughness ($K_{IC}$) of 5.63 and 5.89 MPa·m$^{1/2}$, respectively. The reported densities are 3.16 and 3.2 g/cm$^3$, respectively. Although these two types of balls are similar in appearance and material properties, they differ chemically in the fact that the NBD200 balls are doped with MgO, and the SN101C balls are doped with Y$_2$O$_3$.

The Toshiba balls were manufactured by Toshiba Ceramics. These balls, designated TSN-03NH, possess a slightly higher fracture toughness of 6-7 MPa·m$^{1/2}$. They are also Y$_2$O$_3$-doped balls with a reported density of 3.24 g/cm$^3$. It is also important to note the addition of TiO$_2$ to the Toshiba Si$_3$N$_4$ chemistry. Aluminum and iron are present in all three types of balls with iron being far more prevalent in the SN101C balls. Previous oxidation studies revealed that Al-doped Si$_3$N$_4$ is more
oxidation resistant than Si$_3$N$_4$ without Al (Mukundhan et al., 2002). It has been proposed that the intermediate Al$^{3+}$ cation annuls the abilities of network modifying cations, such as Mg$^{2+}$, to disrupt the random glassy network at the grain boundaries and the amorphous oxide layer that subsequently forms during oxidation of the Si$_3$N$_4$ at elevated temperatures.

Figure 3-1. As-received Si$_3$N$_4$ samples. Pictured from left to right are Toshiba, SN101C, and NBD200. Scale is in inches.

Each of the (0.5 inch diameter) balls was ultrasonically cleansed in acetone, methanol, then deionized water for 10 minutes. When dried, the mass of each ball was recorded five times before being tested in the autoclave.

Preliminary microstructural analysis was conducted by etching the surface of each type of ball. Each sample was placed in molten sodium hydroxide (NaOH) at 450ºC for 20 minutes. The molten NaOH was contained in an alumina boat that was placed on the surface of a hot plate located under a fume hood. The details of the microstructural
analysis of the microstructure are outlined later in the chapter in the scanning electron microscopy section.

Table 3-1. Elemental compositions of Si$_3$N$_4$ additives (in wt.%) of the three types of Si$_3$N$_4$ balls. Compositions were obtained from the manufacturers (Cerbec and Toshiba Ceramics).

<table>
<thead>
<tr>
<th>Element</th>
<th>NBD200</th>
<th>SN101C</th>
<th>Toshiba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.29</td>
<td>0.54</td>
<td>3.3</td>
</tr>
<tr>
<td>Y</td>
<td>-</td>
<td>1.92</td>
<td>3.4</td>
</tr>
<tr>
<td>Ti</td>
<td>-</td>
<td>-</td>
<td>0.79</td>
</tr>
<tr>
<td>O</td>
<td>2.48</td>
<td>3.43</td>
<td>4.4</td>
</tr>
<tr>
<td>C</td>
<td>0.19</td>
<td>0.08</td>
<td>0.12</td>
</tr>
<tr>
<td>Mg</td>
<td>0.52</td>
<td>-</td>
<td>0.011</td>
</tr>
<tr>
<td>Ca</td>
<td>0.01</td>
<td>-</td>
<td>0.012</td>
</tr>
<tr>
<td>Fe</td>
<td>0.03</td>
<td>0.59</td>
<td>0.001</td>
</tr>
</tbody>
</table>

**Hydrothermal Testing**

All hydrothermal tests were performed in a self-sealing autoclave manufactured by Autoclave Engineers. The bench-top assembly consists of a 316L stainless steel pressure vessel surrounded by a ceramic band heater rated 1200 W at 120 VAC. Manufactured by Industrial Heater Corp., the heater is capable of reaching 760ºC (1400ºF). Temperature is controlled by a CT1000 tower controller with a Eurotherm model 2216e temperature controller. Designed specifically to University of Florida specifications, the maximum allowable working pressure of the vessel is 6,000 psi at 427 ºC (800ºF). Figure 3-2 shows the autoclave apparatus which includes the closure assembly, pressure gauge, safety head assembly, valves, and thermocouples. A heat exchanger in the rear of the assembly removes heat via the circulation of cooling water to preserve the vessel.

Once each Si$_3$N$_4$ sample was cleaned and weighed, it was loaded into a stainless steel sample holder which is pictured in Figure 3-3. The circular base of the holder was designed to prevent contact between the sample and the vessel wall. The long stem was incorporated to facilitate the removal of the sample through the top of the vessel. Several
vents were cut through the stem to prevent the disruption of water vapor circulation throughout the vessel. The sample holder was then lowered into the vessel containing the test solution. All test solutions were comprised of deionized water that was purged with air (80% N₂ and 20% O₂) for 3 hours to remove the carbon dioxide (CO₂) and thus any carboxylic acid (CO₂H). Deionized water typically possesses a pH of 5 due to dissolved CO₂. Purging resulted in tests solutions with more neutral pH values (pH≈7). The pH of each test solution was recorded five times with a Thermo Orion model 260A portable pH meter with a Waterproof LM Triode before each autoclave run.

Figure 3-2. Self-sealing pressure vessel manufactured by Autoclave Engineers.
Once the sample was loaded into the vessel, the closure assembly, pictured in Figure 3-4, was used to seal the vessel. The parts used in the closure assembly were the threaded body, cover, seal ring, bearing washer, main nut, thrust washer, lock nut, and set screws. Each part was thoroughly cleaned before each test to eliminate any contamination and to maximize the life of the assembly. The closure assembly provided a metal seal against high pressure through the principle of unsupported area. A tapered seal was created as the main nut was screwed into the body to wedge the seal ring between the dissimilar angles machined into the cover and body. Six hexagonal set screws coated with Jet-Lube SS-30 Pure Copper High Temperature Ant-Seize Lubricant were then tightened to preload the cover into the seal. Pressure end load on the cover then forced each part tightly together.
Figure 3-4. Closure assembly used to seal the autoclave. A self-imposed metal seal is created at approximately 200°C (Drawing provided by Joe Fredrick, Autoclave Engineers).

After the vessel was fastened shut, the control tower was set to heat the vessel to the desired operating temperature. At a temperature of approximately 200°C, the closure assembly sealed itself and pressure in the vessel continued to rise with increasing temperature. Vessel pressure was then controlled through the vent. A ramp rate of 3°C per minute was selected to allow safe control of the vessel pressure through the vent.
Table 3-2. Experimental matrix for the hydrothermal testing of Si$_3$N$_4$.

<table>
<thead>
<tr>
<th>Ball</th>
<th>Temperature ($^\circ$C)</th>
<th>Pressure (psi)</th>
<th>Exposure time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBD200</td>
<td>250</td>
<td>750</td>
<td>6</td>
</tr>
<tr>
<td>NBD200</td>
<td>250</td>
<td>750</td>
<td>12</td>
</tr>
<tr>
<td>NBD200</td>
<td>250</td>
<td>750</td>
<td>24</td>
</tr>
<tr>
<td>NBD200</td>
<td>250</td>
<td>750</td>
<td>48</td>
</tr>
<tr>
<td>SN101C</td>
<td>250</td>
<td>750</td>
<td>6</td>
</tr>
<tr>
<td>SN101C</td>
<td>250</td>
<td>750</td>
<td>12</td>
</tr>
<tr>
<td>SN101C</td>
<td>250</td>
<td>750</td>
<td>24</td>
</tr>
<tr>
<td>SN101C</td>
<td>250</td>
<td>750</td>
<td>48</td>
</tr>
<tr>
<td>SN101C</td>
<td>300</td>
<td>1450</td>
<td>6</td>
</tr>
<tr>
<td>SN101C</td>
<td>300</td>
<td>1450</td>
<td>12</td>
</tr>
<tr>
<td>SN101C</td>
<td>300</td>
<td>1450</td>
<td>24</td>
</tr>
<tr>
<td>SN101C</td>
<td>300</td>
<td>1450</td>
<td>48</td>
</tr>
<tr>
<td>SN101C</td>
<td>325</td>
<td>2000</td>
<td>6</td>
</tr>
<tr>
<td>SN101C</td>
<td>325</td>
<td>2000</td>
<td>12</td>
</tr>
<tr>
<td>SN101C</td>
<td>325</td>
<td>2000</td>
<td>24</td>
</tr>
<tr>
<td>SN101C</td>
<td>325</td>
<td>2000</td>
<td>48</td>
</tr>
<tr>
<td>Toshiba</td>
<td>250</td>
<td>750</td>
<td>6</td>
</tr>
<tr>
<td>Toshiba</td>
<td>250</td>
<td>750</td>
<td>12</td>
</tr>
<tr>
<td>Toshiba</td>
<td>250</td>
<td>750</td>
<td>24</td>
</tr>
<tr>
<td>Toshiba</td>
<td>250</td>
<td>750</td>
<td>48</td>
</tr>
<tr>
<td>Toshiba</td>
<td>300</td>
<td>1450</td>
<td>6</td>
</tr>
<tr>
<td>Toshiba</td>
<td>300</td>
<td>1450</td>
<td>12</td>
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<tr>
<td>Toshiba</td>
<td>300</td>
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<tr>
<td>Toshiba</td>
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<tr>
<td>Toshiba</td>
<td>325</td>
<td>2000</td>
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<tr>
<td>Toshiba</td>
<td>325</td>
<td>2000</td>
<td>12</td>
</tr>
<tr>
<td>Toshiba</td>
<td>325</td>
<td>2000</td>
<td>24</td>
</tr>
<tr>
<td>Toshiba</td>
<td>325</td>
<td>2000</td>
<td>48</td>
</tr>
</tbody>
</table>

After the desired duration of time, the autoclave was switched off and allowed to cool for a minimum of three hours. Then, the vessel was opened and the sample holder was removed. Each sample was allowed to dry overnight before measuring its weight another five times. All test solutions were extracted from the vessel using a pipette which
was thoroughly cleaned after each extraction to prevent contamination. Each solution was stored in a 250mL Nalgene bottle for analysis.

The experimental matrix for the hydrothermal tests is shown in Table 3-2. The primary test temperature of 250ºC was primarily chosen because the pressure vessel must be exposed to at least 200ºC in order to seal itself. Secondly, this temperature (250ºC) is still representative of typical aircraft engine operating temperatures. Higher temperature exposures (300ºC and 325ºC) were performed to determine activation energies.

**Characterization Techniques**

This section outlines the procedures used to characterize the etched as-received Si₃N₄ balls, the Si₃N₄ balls exposed in the autoclave, and the test solutions extracted from the autoclave after each run. The four techniques utilized were scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), pH analysis, and inductively coupled plasma (ICP).

**Scanning Electron Microscopy**

Scanning electron microscopy is a characterization method that focuses a beam of electrons onto a sample that is usually loaded into a vacuum chamber. Electrons in the beam interact with the electrons in the sample. Due to the large energy of the electrons impacting the sample material, x-rays are created which have a characteristic energy corresponding to the position that the electron previously occupied in the electron shell of the atom. Since each element possesses its own specific set of electron shells with specific distances from the nucleus, each element that interacts with the electron beam can be determined by detection of the characteristic x-rays that are produced. These electrons are referred to as backscatter electrons (BSEs) and, depending on the detection equipment, can be used to create energy-dispersive x-ray spectroscopy (EDS) spectra,
backscattered electron images, and elemental x-ray maps. Emitted electrons with energy less than 50 eV are known as secondary electrons (SEs), and their detection is used for sample imaging.

Due to the low electrical conductivity of Si$_3$N$_4$, each ball was mounted on an aluminum mount with a carbon adhesive tab. Carbon paint was applied to approximately 75% of the ball surface to provide a conduit for electrons. If electrons are not able to escape from the sample, a buildup of charge will eventuate. The unpainted portion of the surface of each ball was coated with carbon three additional times using a sputter system. It is this portion that was observed in the scanning electron microscope.

The Si$_3$N$_4$ balls were observed in a JEOL JSM 6400 SEM at the Major Analytical Instrumentation Center (MAIC) at the University of Florida. The surfaces of both the etched and oxidized Si$_3$N$_4$ balls were analyzed using SE imaging, BSE imaging, EDS, and elemental x-ray mapping. Due to the 5 nm resolution of the SEM, any distinct areas that were less than 5 nm in the BSE images could not be isolated by EDS. Elemental x-ray maps were therefore obtained to gain a better understanding of the elemental composition of the ball surfaces. Collection times of 200s and 1200s were allowed for EDS and elemental x-ray mapping, respectively.

**X-ray Photoelectron Spectroscopy**

X-ray photoelectron spectroscopy is a surface sensitive characterization technique that detects electron binding energies. Photons with sufficient energies can ionize an atom when striking the surface of a material, thus producing a free electron that is ejected from the surface. According to the Einstein photoelectric law, the kinetic energy (KE) of the ejected photoelectron is dependent on the energy of the incident photon ($h\nu$). The
Einstein photoelectric law is expressed mathematically in Equation 3-1 where BE represents the binding energy of an electron.

\[ KE = h\nu - BE \quad (3-1) \]

The binding energy can be determined by measuring the kinetic energy of the ejected photoelectron because \( h\nu \) is already known. Simply stated, the binding energy of an electron is the amount of energy required to remove it from the atom (assuming all other electrons do not react to its removal). Since all electron orbitals are discrete and unique to each type of atom, XPS can be used to determine the chemical species present on the surface of a material.

All XPS analysis was conducted using an XPS/ESCA Perkin-Elmer PHI 5100 ESCA System located at the Major Analytical Instrumentation Center at the University of Florida. Modifications to the sample holder were made to accommodate the XPS analysis of the curved ball surfaces. An indentation was made in the bottom of the holder so that the ball could be lowered into it. A flat piece of molybdenum with a circular hole was placed over the top of the ball so that the small amount of ball surface exposed was almost flush with the metal. To accommodate for the metal surface, an analysis of just the sample holder was conducted prior to the Si\(_3\)N\(_4\) sample analysis.

**pH Analysis**

The pH of the test solutions were measured as the first method of chemical analysis. The pH of each test solution was recorded again five times with a Thermo Orion model 260A portable pH meter with a Waterproof LM Triode both before and after each autoclave run. For each measurement, a collection time of five minutes was sufficient to receive a stable reading. Calibration of the pH meter was performed each
week using a set of buffer solutions. Measurements were taken within approximately 12-24 hours after extraction from the autoclave.

**Inductively Coupled Plasma**

Atoms in contact with hot plasma become ionized and emit characteristic light (light of specific wavelengths). Inductively coupled plasma is a characterization technique that utilizes this principle to identify the concentrations of elements dissolved in a solution. The autoclave test solutions were analyzed using a Perkin-Elmer Plasma 3200 Inductively Coupled Plasma Spectroscopy system at the Particle Engineering and Research Center (PERC) at the University of Florida. This system uses argon plasma at 6000ºK and is equipped with two monochromators that cover the spectral range of 165-785 nm. With a detection limit of less than 1 part per million (ppm), the Perkin-Elmer 3200 ICP can also detect multiple elements simultaneously.

The system uses a pump to extract a test solution from a container into the plasma chamber, through a cooling system, and out into a reservoir at a rate of 1 mL/min. As the plasma was warming up, the pump was activated to determine if the proper flow rate could be achieved. After 60 minutes, the volume of deionized water in a graduated cylinder had decreased by 60 mL, and the volume of water in the reservoir had increased the same amount. Instrument calibration could therefore commence.

Calibration of the instrument was performed using multiple standard solutions of the six individual elements listed in Table 3-1 along with a silicon standard solution. Standards of each element (500 ppm and 100 ppm) were created by dilutions of SPEX CertiPrep 1000 ppm standards. Three additional standards containing 0.5, 5, and 50 ppm of each of the seven elements in consideration were also created by dilution. The instrument’s software measured the relative intensities of the light emitted by each
element in the standards of known concentrations to calibrate the instrument using a non-linear regression analysis. A correlation constant of 0.99 was obtained before any testing was to begin.

Each solution test consisted of five replicates, and the mean concentration of each element was recorded. For the autoclave test solutions, the mean concentrations of each element were measured and recorded simultaneously. The system was flushed with deionized water between each run to prevent contamination. To ensure precision, random standard solutions were run after every four autoclave test solutions. It is also important to note that a database of the light wavelengths emitted by each element was consulted before both calibration and testing to ensure that there was no interference amongst the light emitted from each of the elements under investigation. All ICP measurements were performed 1-2 weeks after extraction from the autoclave.
CHAPTER 4
RESULTS AND DISCUSSION

This chapter summarizes the experimental results gained from the hydrothermal testing of Si₃N₄. As discussed in the preceding chapter, the weight of each Si₃N₄ ball was recorded before and after each autoclave exposure. The ball surfaces were analyzed using SEM to both image and characterize the scales that were formed using SE imaging and EDS respectively. Additional analysis of the ball surfaces was provided using XPS. The autoclave solutions were also analyzed via pH and ICP to gain a better understanding of the surface chemical reactions that took place between the Si₃N₄ and the water vapor.

Si₃N₄ Sample Analysis

This section of the chapter presents the weight loss data as well as the SEM and XPS analysis of the ball surfaces. Each ball was visually inspected and photographed before analysis could commence. Generally, each ball turned either light grey or white after each autoclave exposure. Figure 4-1 shows each type of ball after exposure to water vapor at 250°C for only 6 hours. The NBD200 sample now possesses a glossy white finish, indicative of either an adherent silica or silicon oxynitride layer formed on the surface. Samples SN101C and Toshiba appear nearly identical to their as-received counterparts, but appear to have lost a slight amount of their original luster.

The appearance of each ball continued to change as exposure time increased for each temperature. The same degradation of surface luster continued in both the SN101C and Toshiba samples with a chalky, light grey layer forming on the surface. This layer, however, remained adherent after slight handling during both weighing and surface
Figure 4-1. Si$_3$N$_4$ samples exposed in the autoclave for 6 hours at 250ºC. Pictured from left to right are Toshiba, SN101C, and NBD200. Scale is in inches.

Figure 4-2. Si$_3$N$_4$ samples exposed in the autoclave for 48 hours at 250ºC. Pictured from left to right are Toshiba, SN101C, and NBD200. Scale is in inches.
analysis. The NBD200 sample appeared white, but the surface turned chalky and was not completely adherent after only 12 hours of exposure at 250°C. Figure 4-2 shows all three samples after 48 hours of exposure for visual comparison.

**Weight Loss**

All recorded weight changes are reported in mg/cm$^2$ to represent normalized values. These values are necessary for weight change comparisons amongst the three different Si$_3$N$_4$ balls with slightly different diameters. The original diameters of the as-received Si$_3$N$_4$ balls were measured three times using a caliper with the average diameter inserted into the normalized weight change calculations.

Weight losses were observed for all of the Si$_3$N$_4$ samples exposed to hydrothermal conditions. Figure 4-3 gives a comparison of the weight losses amongst the three types of Si$_3$N$_4$ as a function of exposure time at 250°C. The NBD200 samples which contain MgO as its primary additive lost significantly more weight than the Y$_2$O$_3$-doped silicon nitrides.

Figures 4-4 and 4-5 give weight loss comparisons for the SN101C and Toshiba silicon nitrides at 300°C and 325°C, respectively. The weight losses observed for these types of Si$_3$N$_4$ are nearly identical; differing by less than one hundredth of a mg/cm$^2$ at any reported exposure time. Figures 4-6 and 4-7 compare the weight losses observed for the SN101C and Toshiba balls respectively at the three different test temperatures. Each type of Si$_3$N$_4$ lost more weight with increasing temperature for each reported exposure time. The apparent linear weight loss kinetics that was observed will be discussed in the next chapter.
Figure 4-3. Normalized weight loss as a function of time for Si$_3$N$_4$ at 250ºC.

Figure 4-4. Normalized weight loss as a function of time for Si$_3$N$_4$ at 300ºC.
Figure 4-5. Normalized weight loss as a function of time for Si$_3$N$_4$ at 325°C.

Figure 4-6. Normalized weight loss as a function of time for SN101C Si$_3$N$_4$ at various temperatures.
Figure 4-7. Normalized weight loss as a function of time for Toshiba Si$_3$N$_4$ at various temperatures.

**Scanning Electron Microscopy**

The results of the SEM analysis of both the etched Si$_3$N$_4$ samples and the Si$_3$N$_4$ samples exposed in the autoclave are presented in this section. Also included is a comparison of the ball surfaces and microstructures amongst the different ball types. Finally, the results obtained for the Si$_3$N$_4$ samples exposed to hydrothermal conditions will be compared to those obtained for the as-received Si$_3$N$_4$.

**Etched Si$_3$N$_4$**

The microstructure of the etched Si$_3$N$_4$ balls (with no autoclave exposure) was analyzed using SEM. The ball surfaces were prepared using the method outlined in the previous chapter. Figure 4-8 is a secondary electron image showing the microstructure of the as-received NBD200 sample. A backscatter electron image of the same area is pictured in Figure 4-9. Note that the darker regions represent areas that are comprised of
an element or elements possessing a lower atomic number than silicon. These backscatter electron images are not an indication of surface topography. This image also reveals the absence of any regions containing elements which possess a higher atomic number than silicon. Figure 4-10 is an EDS spectrum obtained from the same surface pictured in Figures 4-8 and 4-9. Peaks were obtained for Si, Mg, Ca, and O. Nitrogen peaks are usually absent from the spectra of nitrogen-containing materials, but a small peak appears due to the abundance of nitrogen in Si$_3$N$_4$. Both the Na and Cl peaks are most likely due to the salt contamination that results from human handling and were notably absent from all other EDS spectra obtained in this entire project. Since all of the elements detected by EDS are within 4-5 atomic numbers of one another, there is a lack of compositional contrast in the BSE image that is Figure 4-9.

Figure 4-8. Secondary electron image of etched NBD200 Si$_3$N$_4$ at 5,000X.
Figure 4-9. Backscatter electron image of etched NBD200 Si$_3$N$_4$ at 5,000X. This image was taken in the same region as Figure 4-8.

Figure 4-10. EDS spectrum obtained for the etched NBD200 Si$_3$N$_4$. This spectrum was obtained in the same region as Figure 4-8.
Figure 4-11 is a secondary electron image taken from the surface of the etched SN101C Si$_3$N$_4$ ball at a magnification of 5,000X. A large Si peak appears along with the smaller N and O peaks in the EDS spectrum shown in Figure 4-13. The intensity of the Al peak is several hundred counts greater than that obtained for the as-received NBD200 Si$_3$N$_4$, which is consistent with the greater Al content in the SN101C Si$_3$N$_4$. The presence of Y is indicated by a very small peak at approximately 15 keV. In order to resolve this peak, the accelerating voltage was increased from 15kV to 25kV.

![Secondary electron image of etched SN101C Si$_3$N$_4$ at 5,000X.](image)

Figure 4-11. Secondary electron image of etched SN101C Si$_3$N$_4$ at 5,000X.

From the SE image of the etched Toshiba sample (Figure 4-14) it appears that the beta grains have a slightly higher aspect ratio compared to those in the NBD200 and SN101C Si$_3$N$_4$ samples. Titanium peaks are now present along with a small yttrium peak in the EDS spectra in Figure 4-16. The Al peak is also notably larger than those obtained in the spectra for the other two silicon nitrides. This is also consistent with the relative compositions of Al listed in Table 3-1.
Figure 4-12. Backscatter electron image of etched SN101C Si$_3$N$_4$ at 5,000X. This image was taken in the same region as Figure 4-11.

Figure 4-13. EDS spectrum obtained for etched SN101C Si$_3$N$_4$. This spectrum was obtained in the same region as figure 4-11.
Figure 4-14. Secondary electron image of etched Toshiba Si$_3$N$_4$ at 5,000X.

Figure 4-15. Backscatter electron image of etched Toshiba Si$_3$N$_4$ at 5,000X.
Figure 4-16. EDS spectrum obtained from etched Toshiba Si$_3$N$_4$. This spectrum was obtained from the same region as Figure 4-15.

Si$_3$N$_4$ exposed in the autoclave

The surface morphologies of the Si$_3$N$_4$ balls are shown below in figures 4-17 through 4-19. These SE images (all taken at 5,000X magnification) confirm the formation of a surface layer on the ball surface which was observed in the preceding visual inspection.

Figure 4-20 is a BSE image of the surface of an SN101C ball after 6 hours of exposure at 250ºC. A compositional contrast not present in the as-received SN101C sample reveals the presence of an element with a higher atomic number than Si. An x-ray map, shown in figure 4-21, confirms the presence of iron. A similar contrast is observed on the surface of a Toshiba ball that was also exposed for 6 hours at 250ºC in Figure 4-22. Another look at the surface using x-ray mapping determined that Ti was present on the surface (Figure 4-23). Overall, there appears to be a buildup of Fe on the
Figure 4-17. Surface morphology of NBD200 Si$_3$N$_4$ after 12 hours of exposure at 250ºC.

Figure 4-18. Surface morphology of SN101C Si$_3$N$_4$ after 48 hours of exposure at 250ºC.
Figure 4-19. Surface morphology of Toshiba Si$_3$N$_4$ after 24 hours of exposure at 250ºC.

Figure 4-20. Backscatter electron image showing the compositional contrast on the surface of SN101C Si$_3$N$_4$ after 6 hours of exposure at 250ºC.
Figure 4-21. X-ray map of the surface of SN101C Si$_3$N$_4$ after 6 hours of exposure at 250°C. This map was generated from the same area pictured in Figure 4-20.

Figure 4-22. Backscatter electron image showing the compositional contrast on the surface of Toshiba Si$_3$N$_4$ after 6 hours of exposure at 250°C.
surface of SN101C Si$_3$N$_4$ and Ti on the surface of Toshiba Si$_3$N$_4$ after 6 hours. Neither of these elements are leeching out into solution as indicated by the ICP results presented later in the chapter (and it is presently unclear if solution-reprecipitation occurred). It is important to note that this contrast was not seen in any of the samples with longer exposures. This contrast was most likely masked by the more prevalent oxide scale found on the surface for those samples with longer exposure times.

X-ray Photoelectron Spectroscopy

The XPS spectrum for the molybdenum sample holder is provided in Figure 4-24. All subsequent spectra for the Si$_3$N$_4$ samples have the peaks from the sample holder labeled for clarification. Once the spectra for the Si$_3$N$_4$ ball surfaces were obtained, the Handbook of X-ray Photoelectron Spectroscopy was consulted to reference the observed binding energies. The carbon peak was used as a reference to calculate the shift in the peaks due to the charging that occurred on the surface. The numerical value of this shift
Figure 4-24. XPS spectrum for the molybdenum sample holder.

Figure 4-25. XPS spectrum for NBD200 Si3N4 exposed to hydrothermal conditions at 250ºC for 48 hours.
Figure 4-26. Nitrogen 1s peak for NBD200 Si$_3$N$_4$ exposed to hydrothermal conditions at 250ºC for 48 hours.

Figure 4-27. Silicon 2p$^3$ peak for NBD200 Si$_3$N$_4$ exposed to hydrothermal conditions at 250ºC for 48 hours.
Figure 4-28. XPS spectrum for SN101C Si₃N₄ exposed to hydrothermal conditions at 300°C for 48 hours.

Figure 4-29. Nitrogen 1s peak for SN101C Si₃N₄ exposed to hydrothermal conditions at 300°C for 48 hours.
Figure 4-30. Silicon 2p$^3$ peak for SN101C Si$_3$N$_4$ exposed to hydrothermal conditions at 300ºC for 48 hours.

Figure 4-31. XPS spectrum for Toshiba Si$_3$N$_4$ exposed to hydrothermal conditions at 300ºC for 48 hours.
Figure 4-32. Nitrogen 1s peak for SN101C Si₃N₄ exposed to hydrothermal conditions at 300°C for 48 hours.

BE = 106.8 - 4.5 = 102.3eV

Figure 4-33. Silicon 2p³ peak for SN101C Si₃N₄ exposed to hydrothermal conditions at 300°C for 48 hours.
was subtracted from all subsequent peaks. Nitrogen 1s and Si 2p\(^3\) peaks are enlarged for confirmation. Binding energies for Si sp\(^3\) bonds were referenced which indicated that silicon oxynitride formed on the surfaces of each of the samples analyzed. Peaks for Mg and Y appear for the MgO-doped and Y\(_2\)O\(_3\)-doped silicon nitrides respectively. Although samples exposed to hydrothermal conditions for less than 48 hours still need to be analyzed, this analysis does confirm the presence of silicon oxynitrides on the ball surfaces. It also has established a procedure for analyzing a curved surface.

**Solution Analysis**

In addition to the surface analysis of the Si\(_3\)N\(_4\) exposed in the autoclave, the solutions extracted from the vessel after each test were analyzed. This section discusses the results obtained from both the pH and ICP analytical techniques used in hopes of gaining a better understanding of which Si\(_3\)N\(_4\) constituents are dissolving into solution and which are remaining in the sample. A greater knowledge into the reactions occurring on the Si\(_3\)N\(_4\) surface are also desired and explored.

**pH**

Despite some fluctuations, the pH values of the test solutions increased for all temperatures. This increase in pH is likely due to the emergence of ammonia predicted earlier in Equation 2-2. Initially, the rate of change in pH appears to be rapid; leveling off after 24 hours of exposure. This decrease in rate is likely due to the decreasing hydrogen ion activity with time. It is important to consider the fact that very little ammonia or other ions are needed to shift the pH value of deionized water.

The pH values obtained from the autoclave solutions also correspond with the weight loss data reported earlier in the chapter. Figure 4-34 depicts a larger increase in pH for the NBD200 samples over that of the yttria-doped silicon nitrides after exposure at
Figure 4-34. The pH measurement of deionized water as a function of time after autoclave exposure with various types of Si$_3$N$_4$ at 250ºC.

Figure 4-35. The pH measurement of deionized water as a function of time after autoclave exposure with various types of Si$_3$N$_4$ at 300ºC.
Figure 4-36. The pH measurement of deionized water as a function of time after autoclave exposure with various types of Si$_3$N$_4$ at 325ºC.

Figure 4-37. The pH measurement of deionized water as a function of time for SN101C Si$_3$N$_4$ at various temperatures.
Figure 4-38. The pH measurement of deionized water as a function of time for Toshiba Si₃N₄ at various temperatures.

250°C. At 300°C, the pH values of the yttria-doped silicon nitrides are also nearly identical as are their weight losses. The same is true for the changes in pH observed at 325°C with the exception of the Toshiba solution possessing a more acidic value after 48 hours of exposure. Since the weight loss values between the two silicon nitrides are nearly identical at this time and temperature, the difference in pH could be a result of different additive ions dissolving into solution which will be explored in the next section.

The adsorption of CO₂ gas back into the test solutions may have decreased their pH values.

**Inductively Coupled Plasma**

The results obtained from the inductively coupled plasma solution analysis also correlate with the above weight loss and pH data. At 250°C, the NBD200 solution contains approximately 130 ppm more dissolved Si than either of the yttria-doped silicon
nitrides after 48 hours of exposure (Figure 4-39). After 24 hours, the dissolved Si concentration in the NBD200 solutions appears to reach a limit. This could be either due to the aforementioned lessened activity of H\(^+\), or to the solubility limit of Si in water. It is important to note that the solubility of Si increases with increasing solution pH (CRC Handbook of Chemistry and Physics, 83\(^{rd}\) Ed.). The Si concentrations of the yttria-doped silicon nitrides are also close in values to one another at each of the exposure temperatures (Figures 4-39 through 4-41). Again correlating with the weight loss results, the dissolved Si concentration increased with both increasing exposure time and temperature as depicted in Figures 4-42 and 4-43. The rate of increase in dissolved Si concentration jumps significantly from 250\(^°\)C to 300\(^°\)C. These figures also illustrate the limit in Si solubility in water. One must keep in mind that solubility changes with both pH and temperature. Both of these parameters are changing as the water vapor cools and condenses before solution analysis. Nevertheless, the solution analysis presented is still a good indicator of what is going into solution.

In addition to Si, ICP analysis was also set up to include the detection of the six additive cations listed in Table 3-1. The results are listed in Tables 4-1 through 4-3. Elements with no detected solubility are listed as BDL (below detection limit). The only element that was undetectable for all test solutions was Ti, which was only originally present in the Toshiba Si\(_3\)N\(_4\). Yttrium was only detectable at longer exposure times for temperatures of 300\(^°\)C and 325\(^°\)C.

Calcium and aluminum ions were dissolved in all autoclave test solutions despite Ca not being listed as an additive for SN101C Si\(_3\)N\(_4\). Further research into the ion
sensitive ICP instrumentation revealed that the monochromator is most sensitive to the wavelength that Ca emits when it is ionized by the hot plasma. Whether or not this

Figure 4-39. Silicon concentration as a function of time for Si$_3$N$_4$ at 250°C.

Figure 4-40. Silicon concentration as a function of time for Si$_3$N$_4$ at 300°C.
Figure 4-41. Silicon concentration as a function of time for Si$_3$N$_4$ at 325°C.

Figure 4-42. Silicon concentration as a function of time for SN101C Si$_3$N$_4$ at various temperatures.
sensitivity is extensive enough to affect the detected concentrations on the order of one tenth of a ppm has yet to be determined. On another note, this anomaly also occurs for the detection of Mg ions in the SN101C solutions. A closer look at the EDS spectra for as-received SN101C revealed that the Mg peak could very well have been masked by the Al and Si peaks, thus rendering the peak undetectable by the detection software. Figure 4-44 is an EDS spectra for the surface of as-received SN101C etched for only 10 minutes in molten NaOH. The presence a Ca peak confirms its presence. However, the Mg peak still appears to be masked. All of the SN101C Si₃N₄ additive peaks are clearly defined in Figure 4-45. It now appears that both Ca and Mg are in fact present in the SN101C Si₃N₄, perhaps with concentrations too low to be reported by the manufacturer. It is important to clarify that the primary sintering aid used for the SN101C and Toshiba silicon nitrides is Y₂O₃, while the primary sintering aid in NBD200 Si₃N₄ is MgO.
Table 4-1. Silicon and additive concentrations in autoclave test solutions exposed to the temperature of 250°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (hr)</th>
<th>Si (ppm)</th>
<th>Al (ppm)</th>
<th>Mg (ppm)</th>
<th>Fe (ppm)</th>
<th>Ti (ppm)</th>
<th>Ca (ppm)</th>
<th>Y (ppm)</th>
</tr>
</thead>
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<td>BDL</td>
<td>BDL</td>
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<td>BDL</td>
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<tr>
<td></td>
<td>12</td>
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<td>0.3</td>
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<td>BDL</td>
</tr>
<tr>
<td></td>
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<td>0.5</td>
<td>BDL</td>
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<td>BDL</td>
<td>0.2</td>
<td>BDL</td>
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<td></td>
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<td>0.9</td>
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<td>BDL</td>
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<td>BDL</td>
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<td>BDL</td>
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<td>Toshiba</td>
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<td>5</td>
<td>BDL</td>
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<td>BDL</td>
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<td>BDL</td>
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<td>0.5</td>
<td>BDL</td>
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Table 4-2. Silicon and additive concentrations in autoclave test solutions exposed to the temperature of 300°C.

<table>
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<tr>
<th>Sample</th>
<th>Time (hr)</th>
<th>Si (ppm)</th>
<th>Al (ppm)</th>
<th>Mg (ppm)</th>
<th>Fe (ppm)</th>
<th>Ti (ppm)</th>
<th>Ca (ppm)</th>
<th>Y (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SN101C</td>
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<td>0.2</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>0.2</td>
<td>BDL</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>37</td>
<td>0.9</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>0.2</td>
<td>BDL</td>
</tr>
<tr>
<td></td>
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<td>0.4</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>0.1</td>
<td>BDL</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>179</td>
<td>0.4</td>
<td>BDL</td>
<td>0.1</td>
<td>BDL</td>
<td>0.4</td>
<td>BDL</td>
</tr>
<tr>
<td>Toshiba</td>
<td>6</td>
<td>20</td>
<td>0.1</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>0.3</td>
<td>BDL</td>
</tr>
<tr>
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<td>12</td>
<td>42</td>
<td>0.6</td>
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<td>0.15</td>
<td>0.1</td>
<td>BDL</td>
<td>0.7</td>
<td>0.1</td>
</tr>
</tbody>
</table>

At 250°C, the undetectable Fe and Ti concentrations are consistent with the respective additive buildup observed in the BSE images of SN101C and Toshiba Si$_3$N$_4$.

Note that Fe does dissolve into solution at the longer exposure times for the higher temperatures.
Table 4-3. Silicon and additive concentrations in autoclave test solutions exposed to the temperature of 325°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (hr)</th>
<th>Si (ppm)</th>
<th>Al (ppm)</th>
<th>Mg (ppm)</th>
<th>Fe (ppm)</th>
<th>Ti (ppm)</th>
<th>Ca (ppm)</th>
<th>Y (ppm)</th>
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</thead>
<tbody>
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<td>SN101C</td>
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<td>72</td>
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<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td></td>
<td>12</td>
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<td>0.3</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>0.2</td>
<td>BDL</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>179</td>
<td>0.3</td>
<td>BDL</td>
<td>0.1</td>
<td>BDL</td>
<td>0.1</td>
<td>BDL</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>179</td>
<td>0.6</td>
<td>BDL</td>
<td>0.2</td>
<td>BDL</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Toshiba</td>
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<td>41</td>
<td>0.7</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
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<tr>
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<td>0.2</td>
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<tr>
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<td>0.2</td>
<td>BDL</td>
<td>0.4</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Figure 4-44. EDS spectrum for as-received SN101C Si₃N₄ after only 10 minutes of exposure to molten NaOH.
Figure 4-45. EDS spectrum for SN101C Si$_3$N$_4$ exposed to hydrothermal conditions for 48 hours at 250ºC.
CHAPTER 5
KINETIC ANALYSIS

Linear kinetics was observed for the weight loss which occurred in all three types of Si$_3$N$_4$ balls. Linear rate constants were calculated and are reported later in the chapter. Activation energies for the SN101C and Toshiba balls are also reported in this chapter. Concluding the chapter is a discussion into the possible rate limiting mechanism.

Rate of Reaction

The linear rate constants, $k_l$, were calculated from the slopes of the best fit line for the weight loss data at each temperature for each type of Si$_3$N$_4$ plotted below in Figures 5-1 through 5-7. All of the calculated rate constants are summarized in Table 5-1. The rate of hydrothermal degradation increased with increasing temperature for both the SN101C and Toshiba samples, suggesting an activated process.

Temperature Dependence

Activation energies for the SN101C and Toshiba Si$_3$N$_4$ balls were calculated from the slopes of the Arrhenius plots in Figures 5-8 and 5-9. This Arrhenius relation between the rate constant and temperature is depicted mathematically in Equation 5-1 where $E_a$ is the activation energy, $R$ is the gas constant, $T$ is the absolute temperature, and $A_o$ is a constant.

$$k_l = A_o \cdot \exp(-E_a/RT)$$

(5-1)

When $\ln(k_l)$ is plotted versus inverse temperature, the resulting slope is then equivalent to $-E_a/R$. The activation energies obtained for the SN101C and Toshiba silicon nitrides were 76 and 70 kJ/mol respectively. Therefore, the temperature
Figure 5-1. Linear relationship between weight loss and time for NBD200 Si$_3$N$_4$ exposed to hydrothermal conditions at 250ºC.

\[ k_1 = 1.27 \times 10^{-3} \text{ (mg/cm}^2\text{hr)} \]

Figure 5-2. Linear relationship between weight loss and time for SN101C Si$_3$N$_4$ exposed to hydrothermal conditions at 250ºC.

\[ k_1 = 6.54 \times 10^{-5} \text{ (mg/cm}^2\text{hr)} \]
Figure 5-3. Linear relationship between weight loss and time for Toshiba Si$_3$N$_4$ exposed to hydrothermal conditions at 250ºC.

Figure 5-4. Linear relationship between weight loss and time for SN101C Si$_3$N$_4$ exposed to hydrothermal conditions at 300ºC.
Figure 5-5. Linear relationship between weight loss and time for Toshiba Si$_3$N$_4$ exposed to hydrothermal conditions at 300ºC.

Figure 5-6. Linear relationship between weight loss and time for SN101C Si$_3$N$_4$ exposed to hydrothermal conditions at 325ºC.
dependence on the hydrothermal degradation of the two silicon nitrides is roughly the same. Further testing is needed to determine the apparent activation energy of the NBD200 Si$_3$N$_4$. However, based on the rapid weight loss observed at 250ºC, its hydrothermal degradation will most likely be more dependent on temperature compared to the Y$_2$O$_3$-doped silicon nitrides.
Figure 5-8. Arrhenius relation between linear rate constants and temperature for the hydrothermal degradation of SN101C Si$_3$N$_4$ balls.

Figure 5-9. Arrhenius relation between linear rate constants and temperature for the hydrothermal degradation of Toshiba Si$_3$N$_4$ balls.
**Rate Limiting Step**

The parabolic kinetics associated with the growth of an oxide layer on the surface of Si₃N₄ was not observed in this study. This does not mean, however, that this phenomenon did not occur. Silicon oxynitride scales were observed on the ball surfaces using XPS. Hydrothermal testing for less than 6 hours is still needed in order to prove or disprove the theory of paralinear kinetics that was introduced in Chapter 2. Linear weight loss kinetics, associated with the dissolution of the silica layer was observed in this study. Even if a parabolic weight loss relationship was found before 6 hours of exposure, the long term estimation of rolling element life near engine operating temperatures would be best suited by the linear dissolution model.

From an activation energy standpoint, it does not appear that ion diffusion through the silica either formed at the Si₃N₄ surface or present at the grain boundaries is the rate limiting step in hydrothermal conditions since the solid state diffusion rates are extremely slow at 250-300°C. In addition, the apparent activation energies obtained for the SN101C and Toshiba silicon nitrides are very low compared to those found in the literature for the diffusion of ions through the Si₃N₄ lattice (Schmidt et al., 2004). Even the more open amorphous structure of SiO₂ requires activation energies on the order of 200 kJ/mol for O₂ diffusion and 500 kJ/mol for the incorporation of O₂ into the silica network (Bongiorno and Pasquarello, 2005). Since the parabolic kinetics associated with the growth of a SiO₂ layer and subsequent diffusion of ions through it were not even observed here, it is difficult prove or even to propose the same rate limiting mechanism that was previously proposed by Fox et al. at much higher temperatures; where the rate of degradation in water vapor is limited by the outward diffusion of the additive cations. Since diffusion is a thermally activated process, greater temperatures may allow diffusion
to initially dominate over the dissolution reaction as seen in Fox’s work (Fox et al., 2003).

Since silicates are one of the most abundant materials on earth, their reactions with water are well chronicled in the geochemistry literature. Dissolution reactions of silicates in inorganic aqueous systems involve a number of steps. First, an initial rapid exchange of cations at the mineral surface with protons in solution takes place. Next, an activated complex is formed by what is believed to be a rate-determining hydrolysis reaction (Aagaard and Helgesson, 1982). Finally, the silica and alumina species detach from the remaining surface framework. Overall, this dissolution reaction is a surface-controlled process. The dissolution rate can be expressed by Equation 5-2 where [S] represents the concentration of the surface species in equilibrium with the aforementioned activated complex and k is the rate constant.

$$\text{Rate} = k[S] \quad (5-2)$$

Simply stated, the rate of the silicate dissolution reaction is limited by the amount of adsorbed species at the oxide surface, specifically H\(^+\) and OH\(^-\) (Chou and Wollast, 1984). Kiyoung Kim conducted hydrothermal experiments on CVD Si\(_3\)N\(_4\) at temperatures ranging 250-300ºC (Kim, 2003). He also proposed that the linear dissolution reaction was rate-limited by the surface hydrolysis of a silicate scale.

Referring back to the pH section in Chapter 4, it was proposed that the decrease in the rate of increase in solution pH was due to the decrease in hydrogen ion activity with time (especially considering the closed system used in this project). With all of the chemical processes taking place in the test solution, (i.e., decrease in H\(^+\) activity, increase in NH\(_3\) concentration, leaching of Si and additive cations, the natural decrease in the pH
of water with increasing temperature, and the measurement of the pH being recorded after condensation at room temperature) more studies are recommended before the rate limiting dissolution step can be proven. For example, varying the pH of the initial autoclave test solutions or perhaps more complicated titration experiments to buffer the solutions may become necessary.
CHAPTER 6
CONCLUSIONS

The hydrothermal degradation of three bearing grade silicon nitrides was investigated at 250°C. The MgO-doped Cerbec NBD200 was the least stable of the three types of Si$_3$N$_4$ at this temperature. Two additional exposures at temperatures of 300°C and 325°C were conducted to distinguish between the degradation of the two yttria-doped silicon nitrides as each contained different sintering additives. Dissolution rates followed the linear rate law for all Si$_3$N$_4$ samples at all test temperatures for exposure times ranging 6-48 hours. Apparent activation energies for the Cerbec SN101C and Toshiba TSN-03NH silicon nitrides were calculated as 76 and 70 kJ/mol respectively. More hydrothermal tests on NBD200 are necessary to assess how the MgO-doped Si$_3$N$_4$ performed so poorly compared with the Y$_2$O$_3$-doped silicon nitrides.

All hydrothermal tests were conducted in a self-sealing autoclave. This closed system was used to its full advantage by analyzing the remaining water after condensation. Inductively coupled plasma analysis showed an increase in dissolved Si concentration with time. It also verified the leeching of additive cations into solution. More work still needs to be done to understand the preferential leeching of certain additive cations, but this study provides a good basis since solution analysis on more elements than just Si has not been found in the literature. Solution pH measurements showed an increase in test solution pH with time. Surface analysis of the Si$_3$N$_4$ balls with SEM and XPS provided evidence of SiO$_x$N$_y$ layers.
By way of kinetic and chemical analysis, the proposed rate limiting mechanism for the hydrothermal dissolution of bearing grade Si$_3$N$_4$ is the hydrolysis reaction at the SiO$_x$N$_y$/H$_2$O interface. Thus the concentration of available H$^+$ ions at the amorphous oxide surface also controls the dissolution rate. Therefore, it does not appear that grain boundary dissolution and/or diffusion of additive cations along the grain boundaries is the rate determining step in the hydrothermal degradation of bearing grade Si$_3$N$_4$ at these lower (near operating) temperatures.

A greater understanding of the underlying mechanisms of bearing grade Si$_3$N$_4$ oxidation under hydrothermal conditions is imperative to its detection and prevention. Nondestructive inspections (NDI) instruments and techniques are still under development for corrosion detection in traditional (stainless steel) aircraft bearing systems which have been in use for decades. For corrosion prevention, there is still a significant amount of research and development being conducted for coating development and lubrication optimization. Environmental barrier coatings for the Si$_3$N$_4$ rolling elements will most likely need to be developed to hinder the volatization of the protective silica layer. If further studies into the hydrothermal degradation of Si$_3$N$_4$ can lead to subsequent corrosion detection and prevention in an aircraft engine environment, then catastrophic bearing failures can be eliminated. With no corrosion detection and prevention techniques currently available for traditional bearings, any such techniques developed for Si$_3$N$_4$ will add to the already numerous advantages for its incorporation into an aircraft engine bearing system.


BIOGRAPHICAL SKETCH

Abby Jennings Queale was born in Ft. Lauderdale, Florida, on April 23, 1981. In June of 1999, she earned the International Baccalaureate diploma from Deerfield Beach High School located in Deerfield Beach, Florida. It was at this institution that Abby realized the importance of student and faculty diversity in one’s personal and educational development.

Abby then went on to earn the degree of Bachelor of Science in materials science and engineering summa cum laude at the University of Florida in August 2004. During her undergraduate career, Abby acquired an internship with NAVAIR at the Patuxent River Naval Air Station in Patuxent River, Maryland, where she studied both the corrosion and nondestructive inspections (NDI) of aircraft materials.

In the fall of 2003, Abby joined Dr. Darryl Butt’s advanced ceramics research group at the University of Florida to study the corrosion behavior of bearing alloys in seawater and various lubrications. Soon after, she began her work studying the behavior of bearing grade silicon nitride under hydrothermal conditions.