MULLITE-MULLITE ENVIRONMENTAL BARRIER COATINGS ON SILICON NITRIDE BY COMPOSITE SOL-GEL

by

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Abstract

Silicon nitride is susceptible to paralinear oxidation in applications exposed to combustion environments, such as glow plugs in direct injection natural gas engines. The oxide layer may become volatile in moist high-temperature environments. To protect Si$_3$N$_4$, environmental barrier coatings (EBC) maybe used. Mullite has high corrosion resistance, high temperature strength, and its thermal expansion (CTE=4.5-6 x 10$^{-6}$/°C), is relatively close to that of Si$_3$N$_4$ (CTE=3.3 x 10$^{-6}$/°C). However, the CTEs still differ by a factor of 1.4-2, thus it is difficult to produce crack free EBCs >1 µm thick. To address this, it is proposed that a mullite-mullite EBC be applied by composite sol gel. The addition of calcined powder should reduce the overall shrinkage of the sol, making deposition of thicker (1-5µm) coatings possible. Processing methods to produce mullite-mullite EBC by composite sol gel were studied. Sol gel (SG) mullite precursors were prepared by combining silica-precursor sol with AlOOH sol. Commercially available calcined mullite (CM) was dispersed in the sol, with a solid loading of 36%. Gelation of these sols was studied and it was found that using AlOOH sols at a pH of 2.5 gave the best balance of gelation rate and CM sedimentation rate. Mullite sols were prepared and fired at different temperatures and times. It was determined that mullitization of SG samples required 20min at 1300°C, however, CM addition allowed a similar extent of mullitization at 1250°C. It is hypothesized that the CM acted as seeds, shortening the nucleation step during mullite formation. Calcined samples had a density of 3.01g/cm$^3$, with a total porosity of 9.4%. Glow plugs were dip coated. Final dipping parameters were sol viscosity of 40cps and withdrawal speed of 0.1mm/s. Calcined coatings with CM were relatively crack free with thicknesses of ~3µm. A coated glow plug was tested
on an electric rig for effectiveness against oxidation. After 100hrs at 1300 °C, the
corrosion products layer on the coated glow plug was about one fourth as compared to
the as received glow plugs. In conclusion, the composite sol-gel mullite EBC appears to
provide significant oxidation protection to the silicon nitride glow plugs.
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1 Introduction

1.1 Natural Gas Engines

There has been a lot of push to move towards clean energy for environmental reasons, resource management reasons and also economic reasons. One of these movements is towards the use of natural gas instead of coal or oil. There are plenty of advantages to using natural gas, including combustion engines. From an environmental aspect, natural gas burns much cleaner than diesel and gasoline. Diesel and gasoline include large hydrocarbon molecules, most having formulas $\text{C}_{12}\text{H}_{26}$ and $\text{C}_8\text{H}_{18}$ respectively. The main constituent of natural gas is methane, $\text{CH}_4$, which is the simplest of all carbon chains. Because it is a simple molecule, combustion of natural gas results in fewer intermediate compounds, resulting in lower emissions, including $\text{CO}_2$, unburned hydrocarbons (UHC), $\text{NO}_X$, and particulate matter [1]. Natural gas engines are also efficient. In their current state, they are as efficient as the state of the art diesel engines [2]. However, compared to diesel technologies, natural gas engines have received much less attention and therefore are much less refined. Thus natural gas engines have potential to attain much higher efficiencies than diesel. Also, because natural gas can be essentially used right out of the ground without refining, therefore no by products are generated. From a resource management aspect, switching our dependence on crude oil to natural gas will bring global benefits. Natural gas is much more abundant around the world, including enormous under-sea deposits of methane hydrates which are estimated to exceed 15 quadrillion m$^3$ [3]. Not only are there more reserves of it, unlike oil, they are more evenly distributed around every continent of the world, thus the source of energy supply will no
longer be dependent on a handful of oil deposits [3,4]. From an economic aspect, natural gas cheaper. The production cost of natural gas is lower [5] since the refining process is simpler. And because it is available all on every continent, instead of being in the control of a handful of countries, there should be less competition, resulting in a lesser driving force for its price to go up. On July 15th, 2009, the price of natural gas was US$3.37 per MMBtu compared to the price of crude oil which was US$10.60 per MMBtu [6]. Therefore there is a greater interest than ever to develop reliable efficient natural gas engines.

1.2 Silicon Nitride Glow Plugs and Their Degradation

Currently, many natural gas engines are based upon diesel engines. Diesel engines use compression ignition and require the use of glow plugs during cold starts. During the operation of a diesel engine, air is compressed and the temperature increases. Diesel fuel is injected into the hot air and combusts. During cold starts, glow plugs operating at ~900°C are used to warm up the combustion chamber to ensure that the fuel and air mixture can reach the temperature necessary to combust [2]. The glow plug is turned off after about 10 minutes, when the engine has warmed up to normal operating temperature. In a natural gas engine, the temperature required for ignition is much higher [2]. Thus, rather than being used only to warm up the combustion chamber, the glow plug is used for hot surface ignition. Now operating at 1200-1300°C and constantly in use as long as the engine is running, fuel is sprayed directly at the glow plug, and is ignited at the hot surface. This poses a particular technical challenge. The glow plugs which have been designed to run in diesel engines at lower temperature and for shorter durations are
failing prematurely when used in natural gas engines. The glow plugs are failing after less than 1000 hours of operations, while at least 5000 hours is required by industry (5000 hours of operation is approximately one maintenance interval in the trucking industry) [2].

A collaborative effort between Westport Innovations and the UBC ceramics group has been arranged to investigate the causes of the failure of the glow plugs. It was understood that the glow plugs fail as a combination of several modes of degradation, one of which is chemical degradation. The $\text{Si}_3\text{N}_4$ tip of the glow plugs are subjected to oxidizing and reducing atmospheres in the combustion chamber alternating between fuel and air, and combustion products. Consequently, the $\text{Si}_3\text{N}_4$ is oxidized and the oxide is reduced to volatile species, resulting in gradual material loss. The $\text{Si}_3\text{N}_4$ glow plugs shown in Figure 1-1 were retrieved from a DI-CNG (direct injection compressed natural gas) engine designed and run by Westport Innovations. They show severe levels of material loss after only $\sim 1000$ hrs of operation. It has been proposed that the application of an oxide ceramic coating, such as mullite coating, may offer protection to the $\text{Si}_3\text{N}_4$ glow plug tip from such harsh environments and help in extending the service life of a glow plug. In this study, application of such a coating is investigated. The focus of the currently presented research was therefore on developing the coating material and processing methodologies, and laboratory characterization of the coatings. Such coated glow plugs will be evaluated in simulated (i.e. burner rig) and real engine environment in the future.
Figure 1-1 Used glow plugs retrieved from DI-CNG engines after ~1000hrs of operation showing corrosion and material loss

Figure 1-2 Unused glow plug
2 Literature Review

2.1 Silicon Nitride for High Temperature Applications

Modern industry faces a continually increasing need for materials that can operate for a long time at elevated temperatures. Especially in the field of energy conversion, operation at higher temperatures allows for greater efficiencies and lower particulate emissions (although NO\(_x\) emissions increase). For this reason, components in the hot gas paths are required to be designed to withstand higher temperatures. For example, high temperature superalloys currently used are reaching their temperature limits, thus there is little room for improvement [7]. Ceramic materials are promising alternatives for high temperature applications due to their superior chemical and physical properties. They are capable of maintaining their strength and corrosion resistance at temperatures well beyond the temperature limitations of superalloys. As well, ceramic materials have higher specific strength, allowing moving components to be lighter, also improving the overall efficiency. Silicon nitride, Si\(_3\)N\(_4\), in particular has been a material of interest because of its high melting temperature, high thermal shock resistance, due to its low coefficient of thermal expansion, and relatively good resistance to oxidation and corrosion. It has high flexural strength (up to 1200MPa at 25\(^\circ\)C and up to 550MPa at 1350\(^\circ\)C) [7], high hardness (up to 18GPa Vickers hardness), and low density (3.17 g/cm\(^3\) compared to density of Ni super alloy > 8 g/cm\(^3\))[8]. However, because of its high temperature usage potential, components made of Si\(_3\)N\(_4\) will be subjected to much greater temperatures than current superalloys, where oxidation conditions are much harsher, thus degradation remains to be an important concern.
2.2 Degradation of Silicon Nitride Ceramic

2.2.1 Oxidation of Pure Si₃N₄

What gives Si₃N₄ its excellent oxidation resistance is the formation of a protective film of silica. Since SiO₂ is quite impervious to oxygen, this oxide film acts as an effective reaction barrier. The diffusion coefficient $D$ for oxygen in vitreous silica is $4 \times 10^{-17}$ m²/s at 1200°C [8]. Based on the well known relationship for diffusion distance $x=(Dt)^{0.5}$, it therefore takes $t = 685$ hrs for oxygen ions to diffuse through a $x = 10$ um thick silica film. As some oxygen eventually diffuses through, more Si₃N₄ becomes oxidized, following the reactions: [10].

$$\text{Si}_3\text{N}_4 (s) + 0.75 \text{O}_2 (g) \rightarrow 1.5 \text{Si}_2\text{N}_2\text{O} (s) + 0.5 \text{N}_2 (g) \quad \Delta G = -498 \text{kJ}^a (1)$$

$$\text{Si}_2\text{N}_2\text{O} (s) + 1.5 \text{O}_2 (g) \rightarrow 2\text{SiO}_2 (s) + \text{N}_2 (g) \quad \Delta G = -662 \text{kJ}^b (2)$$

The oxidation of pure Si₃N₄ in pure oxygen takes place in five steps [10]. First, gaseous oxidants transfer to the outside surface of the oxide film. Diffusion through the SiO₂ layer can occur as molecular or as ionic oxygen. Then the above reactions take place at the oxide/silicon interface, and N₂ (g) then diffuses through the oxide film to the surface. Lastly, the N₂ (g) gets transported away from the surface, Figure 2-1.

---

$^a$ ΔG value calculated from ΔG of partial reactions using references [54,55]

$^b$ ΔG value calculated from ΔG of partial reactions using references [54,55]
2.2.2 Oxidation of Silicon Nitride with Sintering Additives

Si$_3$N$_4$ is highly covalent, giving its desirable properties of high temperature strength and hardness and good resistance to corrosion and wear. But these covalent bonds are also responsible for making fabrication processes difficult. Solid-state sintering of Si$_3$N$_4$ powders into dense Si$_3$N$_4$ proves to be nearly impossible. Self diffusivity (in the absence of a concentration gradient) in silicon nitride is quite low ($D < 10^{-19} \text{m}^2/\text{s}$ at 1400°C [11]) and species only become sufficiently mobile for sintering at temperatures above 1850°C where the decomposition of silicon nitride commences [8]. The solution to this is liquid assisted sintering with the use of sintering additives. Additions of RE$_2$O$_3$, or oxides of rare earth (RE) elements, such as erbium, yttrium, ytterbium, and lanthanum can significantly lower the sintering temperature. The melting temperature of SiO$_2$ is ~1730°C [12] but the eutectic temperature of the Er$_2$O$_3$-SiO$_2$, Y$_2$O$_3$-SiO$_2$, Yb$_2$O$_3$-SiO$_2$, La$_2$O$_3$-SiO$_2$ systems is as low as 1680°C, 1660°C, 1650°C, and 1625°C respectively [13],
making sintering possible at much lower temperatures to 97 – 99% of theoretical density [8]

With the use of RE$_2$O$_3$, complications arise in the oxidation process. In additive free Si$_3$N$_4$, the intergranular phases consist of only thin films of amorphous silica. When additives are used, intergranular phases are of different compositions and different mechanisms of oxidation are introduced. If these phases are crystalline, as can be achieved by certain mixes of SiO$_2$ and RE$_2$O$_3$, followed by heat treatment, excellent mechanical properties can be achieved. It has been shown that the combination of mostly crystalline boundary phases and high viscosity glassy films can preserve 90% of room temperature strength at 1300°C [10]. However, due to the lower eutectic temperature and thus lower viscosity of the intergranular film, oxygen diffusion into the material can be considerably higher [10,14]. Refer to Figure 2-2 Schematic of oxidation of Si$_3$N$_4$ with sintering additive [14]. As oxygen penetrates into the bulk material, Si$_3$N$_4$ grains become oxidized to SiO$_2$, increasing the grain boundary phases and enlarging the diffusion paths allowing for increased oxygen diffusion. Further, after the initial formation of surface SiO$_2$ layer, there exist a concentration gradient of RE$^{3+}$ ions between the boundary phases and the surface oxide layer. This driving force causes the outward diffusion of RE$^{3+}$ ions towards the surface oxide layer, which then react with SiO$_2$ and oxygen to form RE$_2$Si$_2$O$_7$ [14]. These reactions which result in the formation of a disilicate layer depend on many factors: amount, distribution, composition, and crystallinity of initial microstructures of secondary phases and intergranular glassy films, cation mobility, and temperature. The consequence of the outward diffusion of RE$^{3+}$ is the change in chemistry and
microstructure of the grain boundary phases, leading to degradation of the bulk Si$_3$N$_4$ material.

![Diagram of oxidation of Si$_3$N$_4$ with sintering additive](image)

**Figure 2-2 Schematic of oxidation of Si$_3$N$_4$ with sintering additive [14]**

For silicon nitride to be used in combustion applications, however, it is important to understand its oxidation behavior not only in oxygen but also in combustion environments. In addition to oxygen, a typical combustion environment is complex, and consists of rapidly changing content of other species including water, carbon dioxide/carbon monoxide, atmospheric nitrogen, hydrocarbon fuels and impurities typically found in such fuels. For the purpose of this work, the focus will only on the first two: water, and carbon dioxide/carbon monoxide.
2.2.3 Oxidation Behavior of Silicon Nitride in the Presence of Water Vapor in Combustion Environment

In a combustion environment, such as inside a land-based or aero-propulsion turbine, or inside a diesel engine, the environment is hostile. Temperatures are upwards of 1200°C. Combustion reaction gases include O₂, H₂O, CO₂, CO, and N₂. Independent of fuel to air ratio, the amount of water vapor remains constant in the vicinity of 10% [15]. Under such conditions, water vapor becomes the primary oxidant of silicon nitride. It has been proposed that the silicon nitride oxidizes according to the overall reaction [15]:

\[
\text{Si}_3\text{N}_4 + 6\text{H}_2\text{O} \rightarrow 3\text{SiO}_2 + 2\text{N}_2 + 6 \text{H}_2 \quad \Delta G = -562 \text{kJ}^c (3)
\]

Others have propose that wet oxidation is in fact the combination of two reactions [16]:

\[
\text{Si}_3\text{N}_4 + 6\text{H}_2\text{O} \rightarrow 3\text{SiO}_2 + 4\text{NH}_3 (4)
\]

\[
4\text{NH}_3 + 5\text{O}_2 \rightarrow 6\text{H}_2\text{O} + 4\text{NO} (5)
\]

In either case has been determined that the oxidation of silicon nitride by water vapor results in a silicon oxide layer, similar to oxidation by oxygen. However, oxidation in the presence of moisture is one order of magnitude faster than in dry oxygen, due to the higher solubility of H₂O in SiO₂ (3.4x10¹⁰ molecules/cm³) compared to the solubility of O₂ in SiO₂ (~5.5x10¹⁶ molecules/cm³) [10]. H₂O disrupts the SiO₂ network, forming non-bridging SiOH groups, permitting faster transport of H₂O, thus allowing for higher

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\[^c\] ΔG value calculated from ΔG of partial reactions using reference [54]
oxidation rates. Similar to oxidation by oxygen, growth of the oxide layer is rate limited by the diffusion of H\(_2\)O through the SiO\(_2\) layer to the bulk Si\(_3\)N\(_4\) material. Thus the reaction rate is parabolic and is proportional to the partial pressure of water vapor [17]:

\[ k_p \propto P_{H_2O}^n \]  

(6)

where \(k_p\) is the rate of parabolic oxide growth and \(n\) is a power-law exponent.

In addition to forming SiO\(_2\) scale by oxidizing Si\(_3\)N\(_4\), water vapor simultaneously reacts with SiO\(_2\), forming volatile species. Many different possible volatile species have been identified, including SiO(g), SiO(OH)(g), SiO(OH)\(_2\)(g), Si(OH)\(_4\)(g), and Si\(_2\)(OH)\(_6\)(g) [7,18]. A study by Opila et al. [18] attempted to determine the primary volatile species from the reaction of SiO\(_2\) and water vapor. The study was done at atmospheric pressure with the partial pressure of water 10\(^{-5}\) to 10\(^{-6}\) bar, and temperature between 1200\(^\circ\)C - 1400\(^\circ\)C. It was determined that the primary volatile species formed is Si(OH)\(_4\), with a high dependence on partial pressure of water vapor, but weak dependence on temperature, according to the equation:

\[
\text{SiO}_2 + 2\text{H}_2\text{O} (g) \rightarrow \text{Si(OH)}_4 (g) \quad \Delta G = -782 \text{ kJ}^d \]  

(7)

The rate of volatilization of SiO\(_2\) to form Si(OH)\(_4\) was determined to be linear [7,17], since the reaction should be limited by the transport of H\(_2\)O and Si(OH)\(_4\) to and from the surface of the SiO\(_2\) scale. Using a flat plate laminar mass transport equation:

\[ \Delta G \text{ value calculated using reference [56]} \]

\[ ^d \]
\[ k_i = 0.664 \text{Re}^{1/2} \text{Sc}^{1/3} (D\rho_v / L) \] (8)

where \( k_i \) is the linear rate of SiO\(_2\) volatilization, \( \text{Re} \) is the Reynold’s number, \( \text{Sc} \) is the Schmidt number, \( D \) is the diffusion coefficient of Si(OH)\(_4\) in the boundary layer gas, \( \rho_v \) is the equilibrium concentration of the volatile Si(OH)\(_4\) and \( L \) is the thickness of the boundary layer. When expanded the equation (8) becomes:

\[ k_i = 0.664 (L\nu \eta / \rho) \nu^{1/2} (\eta / \rho D)^{1/3} (D\rho_v / L) \] (9)

where \( \nu \) is the gas velocity, \( \eta \) is the gas viscosity and \( \rho \) is the density of the boundary layer gas. Within a given system, most of the parameters become constant, and the equation simplifies to:

\[ k_i \propto \nu^{1/2} P_{\text{Si(OH)}_4} / P_{\text{total}}^{1/2} \] (10)

As previously mentioned, the amount of water vapour in a combustion environment remains at around 10% regardless of fuel to air ratio, so it can be assumed that \( P_{\text{H}_2\text{O}} \) is \( \sim 0.1 \ P_{\text{total}} \). Combined with the fact that \( P_{\text{Si(OH)}_4} \) is proportional to \( P_{\text{H}_2\text{O}}^2 \) at equilibrium, from eq (7), the expression further simplifies to [17]:

\[ k_i \propto \nu^{1/2} P_{\text{total}}^{3/2} \] (11)
The linear rate of volatilization then becomes dependent on gas pressure and velocity. For the natural gas direct-injection engine of interest to this work, gas pressure is estimated at about 10-30 atm, and velocity 100 m/s [2]

The formation of Si(OH)$_4$ deteriorates the self protective oxide layer, bringing to question the appropriateness of Si$_3$N$_4$ for extended use in combustion applications. The formation of SiO$_2$ coupled with its removal by the formation of volatile species, causes continual recess of the bulk Si$_3$N$_4$, and is termed “active oxidation” [7]. Over time as Si$_3$N$_4$ parts have been in service inside a combustion environment for long durations, whether the parts will be intact and well protected by an oxide layer, or corroded due to active oxidation will depend on the balance between $k_p$ and $k_l$, eq. (6) & (11). This is also described as “paralinear kinetics” [17]. For example, in the study done by Opila [17], oxidation of silicon carbide is predicted to develop a stable oxide layer of approximately constant thickness of ~0.7 um, or recession into bulk material due to active oxidation (i.e. film volatilization), as shown in Figure 2-3. (In the studies of oxidation of non-oxide silicon ceramics, both SiC and Si$_3$N$_4$ are often used because their behaviors are similar).
In the same study, a model based on $k_p$ and $k_l$ as defined above was developed to map the long term paralinear oxidation and volatilization behavior of SiC, using gas pressure and velocity. The map generated is shown in Figure 2-4, and includes four different oxidation regimes. Regime 1: Negligible Volatilization. At low gas velocities and low pressures, the volatilization rate becomes negligible, thus parabolic oxidation kinetics can be used. Regime 2: Long-Time constant. At even lower gas velocities, and low pressures, the time to reach steady state may be longer than the expected useful life of a component, therefore again parabolic oxidation kinetics can be used. Regime 3: Negligible Volatilization, High Oxidation rate. For low gas velocities and higher pressures, a non-protective oxide layer may form, due to the high oxidation rates. Because the resulting oxide layer is thick and porous, it acts as a poor diffusion barrier for oxidants. Secondly, thick dense oxide layers may also form, however spallation of
the oxide layer becomes a problem. Regime 4: Thin or Missing Oxide Layer. At high velocities and pressures, bare surfaces or thin oxide layers are formed because active oxidation is dominant.

In the combustion chamber of a direct inject compressed natural gas engine, Si$_3$N$_4$ glow plugs are subjected to gas velocities of approximately 100 m/s. During the compression stroke, the pressure is estimated to be 10-30 atm, and even higher during ignition. Thus oxidation would be in or borderline Regime 4 where high gas velocities and high pressures result in a thin oxide layer as evident on the in-service glow plug in Figure 1-1.

Figure 2-4 Mapping of different resulting regimes of parilinear oxidation and volatilization of SiC. Glow plug operations conditions in a DI-CNG engine is indicated by checkered region [17]
2.2.4 Oxidation Behavior of Silicon Nitride in CO – CO$_2$ Atmosphere

Since a significant portion of combustion environments consists of carbon monoxide and carbon dioxide, it is also important to understand the long term behavior of silicon nitride in CO-CO$_2$ systems. In one study [19], the mass change of Si$_3$N$_4$ specimens was monitored in a furnace in an environment consisting of a mixture of CO and CO$_2$ with a total pressure of $10^5$ Pa. The oxidation temperature of the tests varied from 1823K to 1923K (1550°C to 1650°C), the ratio of CO$_2$ to CO ($P_{CO2}/P_{CO}$) varied from $10^{-4.9}$ to $10^{1.1}$, and the total gas flow rates varied from $1.52 \times 10^{-6}$ to $45.8 \times 10^{-6}$ m$^3$/s.

Figure 2-5 Mass loss from active oxidation for $P_{CO2}/P_{CO} < 10^1$ [19]
Figure 2-6 Relationship between rate of mass loss and $P_{CO_2}/P_{CO}$ [19]

The study showed that oxidation of silicon nitride at $P_{CO_2}/P_{CO}<1$ results in linear mass loss due to active oxidation, with the rate being dependent on $P_{CO_2}/P_{CO}$, as shown in Figure 2-5. Figure 2-6 shows the relationships between the rate of mass loss and $P_{CO_2}/P_{CO}$. At the region of $P_{CO_2}/P_{CO}<10^{-4}$, active oxidation rate appeared to be independent of $P_{CO_2}/P_{CO}$. Microscopy on specimens tested at $P_{CO_2}/P_{CO}<10^{-4}$ revealed that the oxidation reaction produced granular graphite like carbon on the surface of the
specimens. No carbon deposit was found on the alumina plates holding the specimens, therefore the carbon on the Si₃N₄ must have been a product of oxidation. With low amounts of CO₂ the main oxidant is CO. The proposed active oxidation reaction is given by the equation:

\[
\text{Si}_3\text{N}_4 + 3\text{CO} \rightarrow 3\text{SiO} + 3\text{C} + 2\text{N}_2 \tag{12}
\]

In the region where \( \frac{P_{\text{CO}_2}}{P_{\text{CO}}} > 10^{-4} \), the active oxidation rate seems to decrease with increasing \( \frac{P_{\text{CO}_2}}{P_{\text{CO}}} \). It was suggested that there is a different oxidation reaction involving oxidation of Si₃N₄ by CO₂, and a different mode of active oxidation by CO. The proposed reactions are given by equations:

\[
\text{Si}_3\text{N}_4 + 6\text{CO}_2 \rightarrow 3\text{SiO}_2 (s) + 6\text{CO} (g) + 2\text{N}_2 (g) \tag{13}
\]

\[
\text{SiO}_2 (s) + \text{CO} \rightarrow \text{SiO} (g) + \text{CO}_2 (g) \tag{14}
\]

As the partial pressure of CO decreases, reaction (14) should be driven to the left and thus the active oxidation rate will decrease, corresponding to trends seen in Figure 4. Eventually when the formation of SiO₂ by reaction (13) exceeds the volatilization of SiO₂ in reaction (14), a stable SiO₂ layer will begin to form. This is supported by the results shown in Figure 2-7. As \( \frac{P_{\text{CO}_2}}{P_{\text{CO}}} > 10^1 \), there seems to be a transition from linear mass loss to parabolic mass gain, indicating the development of a SiO₂ layer.
Figure 2-7 Mass loss from active oxidation for $P_{\text{CO}_2}/P_{\text{CO}} > 10^4$ [19]

Many assumptions and simplifications were made and chosen parameters were different than that of an actual gas turbine, for example, $P_{\text{CO}_2}$ is much bigger in reality. Therefore the studies may not accurately depict what happens to, for example, a real Si$_3$N$_4$ turbine blade. However these results are still valuable because it provides an insight into the behavior of Si$_3$N$_4$ in oxidizing and reducing conditions. The generated models and relationships are likely incapable of correctly predicting the actual outcome of the Si$_3$N$_4$ blade when put into service in a real combustion environment. However, these studies
demonstrate the possibilities of different mechanisms that can occur when Si$_3$N$_4$ is subjected to real combustion conditions. Based on these studies, the understanding of the high temperature performance of Si$_3$N$_4$ is significantly improved. It is now apparent that the weakness of Si$_3$N$_4$ in high temperature applications is the volatilization of the protective SiO$_2$ layer via reactions with either water vapor or carbon monoxide. However, the effects of this degradation may be minimized by the use of environmental barrier coatings (EBC) to protect the SiO$_2$ layer, which is the major objective of the present work.

### 2.3 Application of Environmental Barrier Coatings

One method of improving the performance of Si$_3$N$_4$ is through the deposition of an environmental barrier coating (EBC). If the silica layer can be protected from attack by water vapor and CO, or prevented from being formed, the durability of Si$_3$N$_4$ parts can be significantly enhanced. There are several requirements that must be met in order for a material to be suitable for an effective EBC. Firstly, the EBC material will be subjected to the same conditions as the Si$_3$N$_4$ component itself, so it must have good oxidation resistance up to about 1200°C, good thermal cycling and thermal shock resistance. The EBC must be dense, crack-free and have good adhesion to the substrate so as to be effective in minimizing the diffusion of oxygen and water vapor. Therefore it is critical to minimize the coefficient of thermal expansion (CTE) mismatch between the EBC and the substrate. The coating must be chemically stable and not adversely react with the substrate, compromising the integrity of the component, and also be phase stable within the range of functioning temperatures, because volumetric changes typically
accompanied by phase changes can often lead to cracking. Another consideration is the ease and cost of applying the coating.

Many studies have examined the effectiveness of coating Si₃N₄ with EBC, using a range of materials and methods. Coatings such as alumina from sol gel [20], mullite by plasma spray PS [21], mullite by CVD [22], tantalum oxide by PS [23], and self grown ytterbium silicate coatings [24] have been successfully applied onto Si₃N₄ and have shown different levels of success as an oxidation barrier, or EBC. Alumina (Al₂O₃) is one candidate because of its high chemical stability in many corrosive environments. However, the CTE of alumina (8·10⁻⁶/°C) is significantly larger than the CTE of Si₃N₄ (3.3·10⁻⁶/°C). Mullite (3Al₂O₃·2SiO₂), with a lower CTE (4.5-6 x 10⁻⁶/°C), is more comparable to Si₃N₄. Combined with its good corrosion resistance, mullite has good potential as an EBC. Tantalum oxide (Ta₂O₅) seems attractive as a coating material for Si₃N₄ because of its low CTE (~3.6 x 10⁻⁶/°C), which is essentially the same as the CTE of Si₃N₄. However, Ta₂O₅ has a stable β phase only up to 1360°C [23]. Therefore Ta₂O₅ cannot be used for components that will be exposed to conditions above 1360°C. Another drawback is the cost of Ta₂O₅. Ta₂O₅ powders range from USD$300 - $500 per kilogram.

A novel method was used in a study [24] in which the ytterbium oxide (Yb₂O₃) sintering aid within the Si₃N₄ is used to produce a self grown coating. Under the right conditions, the Yb₂O₃ can react with the silica layer inherent on Si₃N₄ to form Yb₂Si₂O₇. These silicates have been found to be chemically stable and can act as a water vapor barrier.
But little is known about the effects of tapping the \( \text{Yb}_2\text{SiO}_7 \) from the bulk \( \text{Si}_3\text{N}_4 \). It is also unclear whether the integrity of substrate material will be compromised as a result of the reduced bulk levels of the sintering aid. In fact recent work [25] has shown that the \( \text{Yb}_2\text{SiO}_7 \) film forming on \( \text{Si}_3\text{N}_4 \) has poor integrity and is progressively removed in the combustion environment.

Other strategies such as pack cementation coatings have also been examined. Pack cementation has typically been a process used to produce different surfaces on metal components, such as putting a chrome finish on ball bearings. Recently, it has been used to produce an EBC on \( \text{Si}_3\text{N}_4 \) [26]. A component to be coated is embedded inside reactive powders consist of carriers and precursors. Upon heating, the carriers and the precursors will react with the substrate to form the desired coating. The advantage of this process is that it is a diffusion process and thus can produce graded surfaces, and desired chemistries maybe fine tuned by adjusting the constituents of the packing powder. The packing powder formula maybe difficult to optimize and only a small portion of the precursor material actually become coated on the substrate.

### 2.4 Mullite EBC on Silicon Nitride

In this work, mullite has been selected as the coating material to be applied onto \( \text{Si}_3\text{N}_4 \) glow plugs. Mullite is the only compound within the silica (\( \text{SiO}_2 \)) and alumina (\( \text{Al}_2\text{O}_3 \)) binary system, Figure 2-8. Mullite is a stable phase in the composition range of 72 wt% [27] but can be metastable up to 90 wt% \( \text{Al}_2\text{O}_3 \) [28]. Its chemical formula is \( \text{Al}_2[\text{Al}_{2+2x}\text{Si}_{2-2x}]\text{O}_{10-x} \) where \( 0.2 < x < 0.85 \) [29]. Stoichiometric mullite, \( 3\text{Al}_2\text{O}_3\cdot2\text{SiO}_2 \)
(x=0.25), denoted as 3:2 mullite, containing 72 wt% or 60 mol% Al₂O₃, is the only stable crystalline phase at atmospheric pressure above 700°C. Other forms also exists such as 2Al₂O₃·SiO₂ (x=0.4), denoted as 2:1 mullite, containing 77 wt% or 67 mol% Al₂O₃. These forms of mullite are less stable and their compositions gradually shift towards that of stoichiometric mullite at temperatures above 1200°C. Mullite has excellent properties that make it desirable as an environmental barrier coating material for silicon-based ceramics. Compared to Si₃N₄, mullite has higher corrosion resistance, higher creep resistance, and higher high temperature strength and toughness. The relatively good compatibility of the thermal expansion (CTE is 4.5-6×10⁻⁶/°C for mullite vs 3.3×10⁻⁶/°C for Si₃N₄) makes mullite a suitable coating material for Si₃N₄. The thermal conductivity is higher than that of silica (~6 W/mK for mullite vs ~1.3 for SiO₂) [29], and electrical properties are compatible with Si₃N₄ as well (relative dielectric constant ε= 6.7-7.5 for mullite vs. ε= 8.1 for Si₃N₄) [29], which are important for the glow plug application. The most important consideration for EBC, however, is the performance of mullite in corrosive environments.
2.4.1 Mullite in Oxidizing Conditions

Mullite is stable in dry and oxidizing atmospheres so it serves as excellent oxidation and corrosion barriers for Si-based ceramics. For example, Varadarajan et al. found the weight gain for uncoated SiC to be ~12 %, while there was almost no weight gain for mullite coated SiC after 100 hrs at 1300°C in flowing oxygen [30]. Lee et al. found that mullite coatings were not affected after 100 hrs at 1000°C in oxygen and sodium sulfate [31]. Even in static high pressure (10 atm) air environment containing 15% water vapour, Haynes et al. observed no evidence of mullite volatility after 500 hrs at 1200°C [32].
2.4.2 Mullite in Combustion Environments

The presence of water vapour in combustion environments can cause mullite to form volatile hydroxides, predominantly silicon hydroxides [33]. However, as the process begins at the surface, with the release of silica, the substrate becomes enriched in alumina and acts to a certain degree, as a barrier against further mullite decomposition, which explains the higher stability of the mullite compared to Si$_3$N$_4$ in these conditions [34]. Even in a burner rig with 5 ppm sea salt added to the intake air, after 66 hrs at 1050°C there was no corrosion of the mullite-coated Si$_3$N$_4$ [35].

In a study by Ueno et al. [36], it was observed that the decomposition of mullite by the water vapour attack occurred only near the surface of the coating, according to eq 15:

$$5\text{Al}_6\text{Si}_2\text{O}_{13}(s) + 4\text{H}_2\text{O}(g) \rightarrow 3\text{Al}_2\text{O}_3(s) + 2\text{Si(OH)}_4(g)$$  \hspace{1cm} (15)

They also determined that the formation free energy of aluminium hydroxide is higher than that of silicon hydroxide, over the range of 1100-1600°C, again supporting the hypothesis that silica is predominantly removed by water vapour attack. Therefore, silicate compounds such as mullite have generally better corrosion resistance than pure silica.

2.4.3 Mullite in Hydrogen Atmosphere

As for Si$_3$N$_4$, the decomposition of mullite in reducing conditions is mainly caused by the reduction of silica to SiO and its volatilization. Tso and Pask 1982 studied the reaction
with hydrogen of fused silica, aluminosilicate (L) and calcium aluminosilicate (S) glasses in comparison with mullite [37]. The rate of cristobalite reaction with H$_2$ was similar to silica glass and it was assumed that the $\alpha$-Al$_2$O$_3$ did not react with H$_2$; as the total reaction rate of the "L" glass was much lower than for silica glass, it was concluded that the addition of Al$_2$O$_3$ stabilized the silica in the presence of H$_2$. It was explained that in H$_2$ at high temperatures, the increased interactions of the Al atoms with hydroxyl radical and water vapor make the desorption the slowest step, which stabilizes the silica and reduces the total reaction rate. The activation energy of the corrosion reaction with H$_2$ was determined to be 347.3 kJ/mol for silica and 389.1 kJ/mol for mullite, at 1300-1500°C. This is therefore expected that mullite coatings will help to decrease corrosion of glow plugs also in H$_2$ combustion engines. Although such engines are under development at Westport Innovations Inc. (and some preliminary results were generated on glow plug performance), thus is beyond the scope of the present work.
2.4.4 Mullite In CO/CO$_2$ Atmospheres

The equilibrium of silica and mullite in CO/CO$_2$ atmospheres is described by the following equations [38]:

\[
\begin{align*}
\text{SiO}_2(s) + \text{CO}(g) & \rightarrow \text{SiO}(g) + \text{CO}_2(g) \tag{16} \\
\frac{1}{2} \text{Al}_6\text{Si}_2\text{O}_{13} + \text{CO}(g) & \rightarrow \frac{3}{2} \text{Al}_2\text{O}_3 + \text{SiO}(g) + \text{CO}_2(g) \tag{17}
\end{align*}
\]

Reduction of silica by carbon or CO can produce SiO (g), Si(l), or SiC(s), but due to kinetics, only SiO (g) forms below the melting point of SiO$_2$ (1723 ºC). The family of solid-line curves in Figure 2-11 is of log p(SiO) vs $10^4/T$ for the equilibrium of silica in CO-CO$_2$ atmosphere, described by eq (16), with each curve being indexed to a different
value of log \( [p(\text{CO})/p(\text{CO}_2)] \) or “reducing power” of the atmosphere. The family of dash-line curves presents the equilibrium of mullite with CO-CO\(_2\) atmospheres, described by eq (17). As can be seen in the figure, the temperature is about 200°C higher for mullite than silica for equal partial pressure of SiO. The partial pressure of SiO is lower for mullite than silica at any given temperature, indicating that the degradation of mullite will be slower than that of silica.

Figure 2-11 Reduction decomposition equilibria yielding SiO [38]; (solid lines – silica; dashed lines – mullite)
In summary, mullite as an oxide coating offers excellent protection in dry oxidizing environment. Coated specimens showed practically no corrosion of the substrate [30,31,32]. In wet corrosive oxidizing conditions, the formation free energy of silicon hydroxide is lower than that of aluminium hydroxide, giving mullite better corrosion resistance than silica [33,36]. In a H₂ atmosphere, the rate of the corrosion for mullite is lower than silica, giving mullite greater durability [37]. In a reducing environment containing CO and CO₂, the reactions from solid SiO₂ into gaseous SiO are slower for mullite than silica at the same temperature [38]. This superior corrosion resistance of mullite to silica can be translated to the case of coated Si₃N₄. Considering that the basis of the corrosion of Si₃N₄ is the corrosion of its passive silica layer, mullite will also have better corrosion resistance than Si₃N₄. Therefore, coating Si₃N₄ with dense, adherent and uniform mullite should offer increased protection from corrosive environments.

### 2.5 Processing of Mullite

Mullite (3Al₂O₃·2SiO₂) can be formed by heating and decomposing aluminosilicates such as andalusite and sillimanite (both are Al₂O₃·SiO₂). It is also the main constituent in porcelain that is formed through the decomposition of kaolinite (2Al₂O₃·3SiO₂). Traditionally, mullite is formed by reaction sintering of well-mixed alumina and silica powders. Synthesis of mullite from powders however requires high temperatures and relatively long time. For example, it has been reported that mullitization of quartz and α-alumina powder was complete only after 8hrs of heat treatment at 1700 °C [29]. Such long process times are necessary because Al₂O₃ and SiO₂ are required to diffuse into each other before mullite formation, and the diffusion coefficients are low. For example, the
diffusion coefficient of silicon and aluminum in mullite at 1400 °C have been measured to be in the order of $10^{-20}$ m$^2$/s [39] and $10^{-18}$ m$^2$/s [40] respectively. High temperature processing is obviously associated with higher energy and equipment costs. Mullite can also be produced by sol gel processing, which is a lower temperature alternative, explored further in the following sections.

### 2.5.1 Sol Gel Processing

Sols are stable colloidal suspensions of solid particles on the order of 1 - 1000 nm in size. In this range of size, gravitational forces have minimal effect and short range forces such as van der Waals forces and ionic attraction become dominant. There are two types of sol precursors: particulate sols and polymeric sols [41]. Particulate sols are created by dispersing metal oxides in water. Metal oxide particles develop a surface charge when submerged in water. Depending on the acidity of the solution, either H+ or OH- ions adsorb onto the surface of the particles creating a surface charge. This surface charge attracts counter ions which form a layer of opposite charge surrounding the particles creating a double layer. The magnitude of the charge at the double layer is quantified by the zeta potential. The outer layer of counter ions causes particles to repel each other while van der Waals forces pull particles together. This balance of attraction and repulsion keep particles well suspended [41]. A sol is considered to be stable when the zeta potential is greater than ±30 mV. When the zeta potential is less then ±30 mV, and close to the isoelectric point, particles lose their surface charge and the double layer. Inter-particle attraction due to van der Waals forces causes flocculation, forming a network, gel.
Polymeric sols are created by dissolving organo-metallic compound such as alkoxides into water and/or alcohol. Through the hydrolysis and polycondensation of alkoxide molecules, polymers are formed and are well suspended in the solvent. These inorganic polymers can become further networked, eventually forming macromolecules [41]. Whether particulate or polymeric, a structure is formed from the network in the sol, creating a gel. When a sol becomes a gel, it develops rigidity and shape retention ability. Such gels can then be dried and heat treated for densification and crystallization to create the final ceramic material.

2.5.2 Advantages of SG Processing

Sol gel processing has several advantages. The main advantage is the high purity of sol gel derived materials. Because sols are prepared using chemical precursors, very pure final materials can be attained. For example, since mechanical processing such as ball milling is unnecessary, contamination by the milling medium is avoided. Commercial mullite powders derived from traditional powder processing typically contain 1.6wt% impurities while sol gel derived mullite powders contain as little as 0.05wt% impurities [29]. These impurities include oxides like Na$_2$O, Fe$_2$O$_3$, and CaO, which can significantly reduce high temperature properties of mullite. Another advantage is the relatively low temperature of most stages of sol gel processing. Sol processing is done at ambient temperatures, gel drying is done at about 80°C. When producing materials requiring sintering, such as mullite, heat treatment times and temperatures are also reduced compared to traditional powder processing. Sintering temperatures of traditional
powder processing of mullite are usually above 1750°C while most sol gel processing of mullite require less than 1300°C [29]. Unlike in powder processing where the aggregates are usually on the order of 10µm in size, the particles suspended in the sols are on the order of 1µm in size, or less. This allows for a level of intimate mixing of precursors not achievable in powder processing. Because precursors are better mixed, diffusion paths of alumina and silica into each other are shorter (in the nanometer range) and mullitization is achieved much more rapidly. Complete mullitization of diphasic gels, are reported to be at <1300°C, some in as little as 1 hr, while mullitization of monophasic gels can be below 1000°C [29]. Such reduced calcination time and temperatures translate into significant energy savings when implemented commercially. The important advantage of sol gel processing is its application towards thin film fabrication. Prior to gelation, sols can be used for thin film coatings by methods such as dip coating and spin coating. Uniform coatings of high purity between 5 – 500 nm can be easily deposited [41]. In this work, however, we are interested in thicker coatings, in several µm range.

2.5.3 Mullite by Sol Gel Route

Precursor preparation of sol gel derived mullite can vary, but in general two precursors are mixed together: one as the source of silica and one as the source of alumina. Commonly, a silicon alkoxide such as tetraethylorthosilicate (TEOS), Si(OC₂H₅)₄, is used as the source of silica [29]. A TEOS molecule has a Si ion with four ethyl groups attached. When exposed to OH⁻ ions, TEOS hydrolyzes, where an OH⁻ replaces an ethyl group [41]:

$$\equiv \text{Si} - \text{OC}_2\text{H}_5 + \text{HOH} \rightarrow \equiv \text{Si} - \text{OH} + \text{HOC}_2\text{H}_5$$

(18)
When hydrolized to greater than 2 degrees (2 or more ethyl groups replaced by OH), TEOS molecules bond together through condensation:

\[
≡\text{Si} - \text{OH} + \text{HO} - \text{Si} ≡ → ≡\text{Si} - \text{O} - \text{Si} ≡ + \text{HOH} \quad (19)
\]

Further condensation creates polymer chains that establish the network of Si and O in the resulting sol and gel.

\[
≡\text{Si} - [\text{O} - \text{Si} - \text{O}]_n - \text{Si} ≡ \quad (20)
\]

As the source of alumina, boehmite AlOOH is a common precursor. At a pH of above or below the IEP of boehmite (pH~9), particles of AlOOH is suspended by a double layer, producing a particulate sol [41]. A gel produced using such precursors would be a diphasic gel, because it incorporates a polymeric sol and a particulate sol. Subsequent to gelation and drying, calcination would lead to mullitization.

Heat treatment of sol gel mullite precursors brings about several stages. At 100°C - 120°C there is final removal of solvent along with the burnout of residual organics. At above 400°C dehydroxilation of boehmite according to the equation (21) and condensation of Si(OH)$_4$ according to the equation (22) result in the production of $\gamma$-alumina and amorphous silica, and further removal of water [29,41,41]:

\[
2\text{AlOOH} → γ\text{-Al}_2\text{O}_3 + \text{H}_2\text{O (l)} \quad (21)
\]
\[
\text{Si(OH)}_4 \rightarrow \text{SiO}_2 + 2 \text{H}_2\text{O (l)} \quad (22)
\]

As temperature increases, the densification process is driven by the reduction of the high surface energy of pores. At 1250°C mullitization begins by a period of nucleation at the interface between $\gamma$-alumina and silica, at a nucleation density of about $2 \times 10^{11}$ cm$^{-3}$, followed by grain growth and continued nucleation [29].

### 2.5.4 Disadvantages of Sol Gel Processing

The greatest drawback to sol gel (SG) processing is the relatively large shrinkage associated with drying and sintering (for example, there is ~70% volume reduction for silica sols) [43]. As a sol becomes a gel, networks form and the gel develops rigidity. Initially the gel submerged in the solvent has solid liquid interfaces. As solvent leaves the system, the gel becomes exposed, introducing higher energy solid vapor interfaces. To reduce the energy of the system, solvent contained with the pores of the gel is drawn to the surface of the gel retaining the solid liquid interface. This driving force continually draws solvent out of the system. Capillary pressure in the pores becomes the main acting force for the shrinkage of the gel [41]. During thin film processing, resultant tensile stress on the gel can become great enough (up to 180 MPa [44]) to cause collapse of the structure of the gel dense coatings. However, SG coatings are usually limited to thicknesses of less than 1μm. It is difficult to obtain coatings thicker than a few μm because drying stresses are large enough to result in crack formation. Shrinkage leads to cracking that exposes the substrate.
2.6 Dip Coating

Dip coating is a common coating technique used in applications such as optical coatings and membranes. During the dip coating process, the substrate is submerged into the sol and precisely withdrawn out of the sol [45]. The coating is the deposited film of sol that adheres to the part. During the gelation stage of a sol, suspended particles begin to hydrolyze, bonding with one and other. As networks begin to form, the degree of gelation increase and as does the viscosity. Eventually, the sol becomes completely gelled. The speed at which this happens is influenced by pH of the system as both the attraction between particles and hydrolysis are affected by the H\(^+\) and OH\(^-\) ions in the system [41]. By studying the gelation behavior over time and the affect of pH, one can gain control over the viscosity of the sol. Then, applying a coating of desired thicknesses on a part becomes relatively straight forward. The thickness of the coating applied by dip coating can be given by the Landau and Levich formula [46]:

\[
h = 0.94 \frac{(\eta \cdot v)^{2/3}}{\gamma_{LV}^{1/6} (\rho \cdot g)^{1/2}}
\] (23)

When dip coating with a given medium, \(\gamma_{SL}\) the solid liquid surface tension, \(\rho\) the density, and \(g\) gravitational acceleration, are constants, Therefore, one can achieve desired a coating thickness \(h\) by careful control of viscosity \(\eta\) and withdrawal speed \(v\).
2.7 Composite Sol Gel and Seeded Sol Gel Processes

In Composite Sol Gel (CSG) processing, inert ceramic filler is dispersed into conventional SG precursors during processing [47]. The filler material is one which is already calcined, and thus will no longer shrink during further processing and heat treating, and should also have a minimal impact on the coating chemistry and performance. When the dispersed powder becomes a significant fraction of the sol, large strains of conventional sol gel films, upon heating and densification, are reduced due to the reduced overall shrinkage of the sol. This reduction in shrinkage allows for thicker film coatings to be deposited while remaining crack free [47]. If the dispersed powder is the same material as the bulk material, then the resulting CSG material should have properties comparable with those of the bulk material. This method has been shown in the study by Barrow [47] to be successful in a variety of coatings including cesium stabilized zirconia, titania, silica and alumina containing up to 50wt% filler. Processing of mullite coatings by this method should therefore also a viable option to produce thick dense coatings, such as one which is suitable for applying onto Si₃N₄ glow plugs. However, there are no literature sources available on mullite-mullite CSG.

Furthermore, if the dispersed ceramic filler in SG has a fine particle size, seeding effects maybe realized. Seeded sol gel processing involves the addition of fine crystalline seeds to promote crystal growth or transformations. Kumagai and Messing examined the effects of seeding in sol gel alumina processing by dispersing alpha alumina seeds (0.1µm) into boehmite sol [48]. The addition of the seeds lowered the θ to α alumina transformation temperature by 170°C, increased the kinetics of transformation by
providing nuclei for the transformation, and increased sintered density. Similar results were obtained by Anilkumar et al. in a study of seeded sol gel mullite processing [49]. The presence of mullite seeds promoted earlier formation of the mullite phase, which was observed in seeded samples at 1200°C compared to 1300°C required by the unseeded samples. The final sintered density was also enhanced. In addition, Mroz and Laughner demonstrated that the addition of seeds can be used as a method to control the final sintered microstructure [50]. However, as these studies were seeding studies, only relatively small amounts of powders were added as seeds (0.125 wt% to 10 wt%) and only the affect on crystallization were examined in non coating applications; the effect on shrinkage reduction was not addressed. In this work, we explore much larger contents of calcined mullite (>30wt%) in sol gel mullite.
3 The Rationale, Scope and Objectives

3.1 Rationale and Scope of the Research

There has been little work done on the coating of Si$_3$N$_4$ with mullite via sol-gel method. Most studies that investigate into mullite coating on a Si$_3$N$_4$ substrate focus on plasma spraying of mullite, likely due to the greater coating thickness achieved by plasma spraying, and larger areas for coating (e.g. turbine blades). There are fewer applications where, small Si$_3$N$_4$ parts need a thin coating. Researchers studying dense mullite thin films for academic purposes have typically produced them by chemical vapor deposition (CVD). But CVD is expensive, and size and geometry of a part can be limited by the reactor.

In the case of the Si$_3$N$_4$ glow plugs, coating them with plasma spraying technique would not be viable, because plasma spraying results in coatings that are too thick (typically >20um) and porous (typically >10vol% porosity). For a coating to function well on a glow plug, it would have to protect the hot tip from its surroundings, but would also have to be minimally thermally insulating. If the coating reduces the hot surface temperature of the hot tip, the glow plugs functionality would be affected. It maybe possible to increase the glow plug temperature to counter the insulating effect of thick porous coating, but that would be counter intuitive to the intent of extending the service life of glow plugs. Also, because they are designed to be used inside the combustion chamber, dimensional tolerances are very tight. Therefore, the coating for Si$_3$N$_4$ glow plugs will have to be thin (preferably <10um) and dense (preferably >95% of theoretical density).
Application of such coatings via CVD is difficult due to the complex geometry of the glow plug. It would be very difficult if not impossible to coat just the hot tip of a glow plug in a reaction chamber. Applying a uniform coating all around the cylindrical surface of the hot tip may also pose a challenge. Not to mention, coating each glow plug using CVD is impractical due to high processing cost.

Producing mullite coatings via sol gel route seems promising due to its relatively low temperature, possibly below 1200°C, and ease of processing. However, an optimal coating may be difficult to obtain. If too thick, the sol gel coating maybe prone to cracking from drying. To minimize stresses developed from evaporation of solvent, the use of thinner coatings maybe necessary. However, if the coating is too thin, it may prove to be ineffective. Layering of several thinner coatings maybe feasible, but can introduce other issue of adhesion between consecutive coats. Multiple coating also significantly increases processing time and cost. Currently, there is not a well developed process to deposit dense mullite coatings of sufficient thickness (>2 µm) in a low cost and robust manner. Such a process would be appropriate for applications similar to an EBC for the Si₃N₄ glow plug. Study and development of such process is the primary objective of the present work.

It was proposed in the present work that, despite the shrinkage problems associated with sol gel (SG) processing, coating Si₃N₄ with dense and sufficiently thick (>2µm) mullite from sol gel remains to be a viable option. It appeared that the shrinkage issue was the main hurdle to overcome in order to apply dense mullite coatings on objects such as
Si₃N₄ glow plugs. To lessen the effect of shrinkage, it was proposed that Composite Sol Gel (CSG) technology can be used.

It was hypothesized in the present work that by using an increased amount of fine calcined powder, they can act as both seeds and filler, allowing both the benefits of CSG processing and seeded sol gel processing to be realized. Fine calcined mullite powder (<1μm particle size) has been selected as a filler for SG precursors for the coatings. This has the advantage of creating a final material composed of mullite filler in a matrix of bulk mullite, with no overall change in system chemistry. There should be no CTE mismatch between the filler and bulk, thus sources of stress are not introduced into the system with the addition of the filler. Because fine mullite powder was used, it was expected to act as seeds providing nucleation sites for the formation of SG-derived mullite. Additionally, a powder with a fine particle size is necessary to ensure that they are well dispersed and incorporated into the bulk mullite precursors. Finer particle size allows the calcined particles to be better suspended during sol processing; hence the selection of a mullite powder with <1μm particle size. Minimization of processing shrinkage of SG films in general remains a challenge and this work is to demonstrate that this challenge could be addressed through the use of Composite Sol Gel (CSG). In combination, the concept of seeding could be used to reduce calcination times and temperatures.

The scope of this project includes process development for mullite-mullite CSG in bulk and coating forms. The development of mullite phase in such bulk composite has been
investigated (SEM, XRD, TGA/DTA) relative to time and temperature of the heat treatment, and calcined mullite addition. Once a process for bulk CSG has been achieved, the process to deposit coatings of such materials has been investigated and optimized. Extensive SEM characterization of the resultant families of coatings on various substrates followed. Finally, the target ceramic (Si$_3$N$_4$) glow plugs were coated and delivered to the industrial partner (Westport Innovations) for evaluation of the coatings effects on the lifetime of glow plugs in simulated and real engine environments.

### 3.2 Objectives of the Research

The four main objectives of this project are:

1. **Investigation of the process to achieve composite sol gel (CSG) mullite in bulk** – The study of bulk CSG systems was performed to gain an understanding of mullite development and to determine how to carry out the process in a controlled manner.

2. **Application of CSG mullite coating on Si$_3$N$_4$ forms** – Once an understanding of mullite development has been obtained, it lead us towards an investigation into the application of composite sol gel mullite as a coating. Experiments have been set up to understand different factors that can affect the coating process, to gain control of the coating process, and to develop a feasible process to apply dense mullite coatings of adequate thickness (> 2 µm) onto Si$_3$N$_4$ substrates.

3. **Investigation of microstructure and morphology of such processed mullite ceramics** – CSG mullite in bulk and in coating form were characterized extensively using SEM, XRD, TGA/DTA.
4. Evaluation of CSG mullite coated glow plugs – The final applied objective of this collaborative project is the evaluation of such CSG mullite coated glow plugs in DI-NG and H\textsubscript{2} environments, both simulated and in real engine testing cell at Westport Innovations Inc. Simulated engine environments include electric rig, burner rig and engine rig testing. As the tests are underway during writing of this Thesis, only early testing results are provided.
4 Methods

4.1 Characterization Techniques

Thermal characteristics of the sols were investigated by thermogravimetric analysis, TGA, in a thermal balance (Linseis L81/1750). Samples were heated up to 1500°C at a rate of 10°C/min in still air. For the phase development study, crystallographic investigation was done by x-ray diffractometry, XRD, (Rigaku Multiflex 2kW, Japan). Samples were prepared by grinding in mortar and pestle using ethanol as lubricant. Powders were dried in a drying furnace maintained at 65°C. XRD spectrums were collected at 2°/min over a diffraction angle 2θ range of 20°-80° and were analyzed using Jade 5.0 software. To determine the effect of the coating procedures, surfaces morphology of samples were investigated by electron microscopy, SEM, (Hitachi S-3000, Japan). Samples were analyzed under variable pressure (20kPa) with a electron beam power of 20kV. Analysis was performed in backscatter mode to avoid the need to carbon coat samples in order to minimize the amount of contamination and surface alterations of samples through additional processing and handling. Sample chemistry was determined by energy dispersive x-ray spectroscopy, EDX, (Quartz XOne, Canada).

4.2 Preparation of Mullite Precursors

Mullite was prepared by mixing two precursor sols. To obtain the alumina portion of mullite, boehmite (AlOOH) was used. 0.5 molar boehmite solution was prepared by mixing boehmite powder (Disperal Sol P2, Condea Chemie GmbH, Germany) into
distilled water prepared using a Megahome MH943 water distiller. Distilled water was used because minor impurities can affect sol gel processing. The solution was then mixed using a Horiba HA500 ultrasonic disruptor probe for 10 min to eliminate any agglomerations. The solution was stirred on a hot plate and maintained at 70°C for 12 hours, then cooled to room temperature before use, Figure 4-1. To obtain the silica portion of the mullite sol, 98 wt% tetraethylorthosilicate, TEOS (Sigma-Aldrich Chemicals, USA) was used. 11.2 ml of TEOS was added to 23.2 ml of denatured ethanol and mixed using a magnetic stirrer for 20 min. 2.5 ml of concentrated HCl (33 wt% in water) was added drop wise to partially hydrolyze the TEOS and stirred for another 20 min. The TEOS sol was used immediately after preparation, Figure 4-2. To make the mullite sol with no calcined mullite (CM) addition, stoichiometric proportion of TEOS sol is added drop wise and mixed into the boehmite sol; for example, to obtain one batch of such mullite sol precursor, 100 ml of boehmite sol was combined with 11.6 ml of TEOS silica sol. This mix is denoted as SG, Figure 4-3.

To prepare the sol with filler, fine calcined mullite powder (MULSM Baikowski, USA), with a \( d_{50} \) particle size of 0.74 \( \mu \)m, was first dispersed in the boehmite sol prior to mixing with the TEOS sol. To ensure the CM particles are well suspended, it is important to ensure that the pH of the sol is away from the isoelectric point (IEP) of mullite. This is also true for boehmite. From Figure 4-5 and Figure 4-6 it can be seen that at a pH of below 7.2, the system is below the IEP of both mullite and boehmite. To maintain good dispersion of powders, their zeta potential should be at least \( \pm 30 \) mV, therefore, the pH range of below 6 was chosen for this study. The pH of the boehmite sol was adjusted to
Figure 4-1 AlOOH sol preparation

Figure 4-2 TEOS sol preparation

Figure 4-3 preparation of SG sol

Figure 4-4 preparation of SGCM sol
1.5 to 6 by the addition of HCl. 1.78 g of CM mullite was subsequently added into 100 ml of the pH adjusted boehmite sol. The sol was then ultrasonicated with the ultrasonic probe for 10 min to disperse the CM powder and to break up any agglomerates. As before, 11.6 ml of TEOS was then added drop wise into the boehmite sol with the dispersed CM to obtain stoichiometric proportions. This mix is denoted as SGCM. The sol preparation process is outlined in a flow chart in Figure 4-4.

Figure 4-5 Zeta potential vs pH for boehmite [51]
The calcined mullite (CM) filler was examined under the SEM, shown in Figure 4-7. The particle sizes appear to be in accord to manufacture specifications. The analysis report from the manufacture indicated that the powder had d20, d50, and d90 sizes equal to 0.21 µm, 0.79 µm, and 4.3 µm respectively. Evident in the micrograph, agglomerates were present and hence the need to use an ultrasonic disruptor probe during sol processing. The chemistries gathered using EDX is shown in Table 4-1. Stoichiometric 3:2 mullite should theoretically contain 48.8 wt% Al, 13.19 wt% Si, and 48.80 wt% O, yielding a wt% ratio of Al:Si is 2.88. The ratio of 3.30 obtained from measured values of the as-received CM powder indicates that it may be alumina rich, containing a mix of 3:2 mullite and 2:1 mullite. This ratio was used later to gauge relatively whether prepared mullite samples are close to stoichiometry, silica rich or alumina rich. The analysis
report also indicated that the phase constituents of the calcined mullite powder should contain 98 wt% mullite and less than 2 wt% of other phase (silica and alumina).

The XRD spectra of the as-received CM powder and the same powder heat to 1300°C for 1 hr are shown in Figure 4-8. Large well defined peaks confirm the predominant phase to be mullite, while much smaller cristobalite and corundum peaks detected correspond to the 2 wt% of other phases. The heat treatment at 1300°C for 1 hr did not lead to any changes in the XRD spectra, verifying that the CM powder is inert and is suited to act as inert filler for composite sol gel processing. The addition of 1.78g of calcined mullite filler in each batch is equivalent to 36 wt% in the final calcined product. In the preliminary work, sols with higher CM loading were also prepared. However, samples containing 70 - 90 wt% CM filler resulted in poor sinterability in the final product, and their sintered strength was similar to that of dried gel. The higher fraction of filler may have resulted in poor bonding between the sol gel matrix and CM filler, leading to poor sinterability. On the other hand, the samples with 20 wt% CM filler sintered well, but had no observable reduction in shrinkage. In the end, 36 wt% of CM in the sol was considered to be most suitable for this study.
Figure 4-7 Micrograph of as received CM powder

<table>
<thead>
<tr>
<th></th>
<th>O</th>
<th>Wt %</th>
<th>Al</th>
<th>Si</th>
<th>Al:Si ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>CM only</td>
<td>55</td>
<td>34</td>
<td>10</td>
<td></td>
<td>3.3</td>
</tr>
<tr>
<td>3:2 Mullite theoretical values</td>
<td>49</td>
<td>38</td>
<td>13</td>
<td></td>
<td>2.8</td>
</tr>
<tr>
<td>2:1 Mullite theoretical values</td>
<td>30</td>
<td>25</td>
<td>6.6</td>
<td></td>
<td>3.8</td>
</tr>
</tbody>
</table>

Table 4-1 Average compositions of as received calcined mullite powder, as compared with theoretical values

Figure 4-8 XRD patterns of SG, SGCM and CM after calcination at 1300°C for 1hr.

- mullite, □ corundum, x cristobalite
4.4 Calcined Samples for Phase Development Study

Both SG and SGCM samples were dried for 48 hrs in a covered crystallization dish in a drying oven at 65°C. TGA was performed on a portion of the dried SG and SGCM specimens to examine their calcination behavior. The remaining dried specimens were calcined at 1200°C - 1400°C, for 20 min - 9 hrs. Ramping rate of the furnace was set to 8°C / min. Calcined samples were checked for phase content by XRD, and also examined by SEM and EDX. Measured wt% ratio of Al:Si are compared to the theoretical values to gauge the relative degree of stoichiometry in the samples. Densities were measured by the displacement of water using 25ml glass pycnometers. The mass of dry samples are recorded. Then the samples were submerged in water and boiled under a vacuum for 30 minutes to remove air within open pores. With the pycnometers filled up, samples were weighed again. The difference in weight is the amount of water. The density of the sample is then given by:

$$\rho = \frac{\text{Mass}_{\text{dry}}}{(25\text{ml} - \text{VolH}_2\text{O})}$$  \hspace{1cm} (24)

Closed porosity is given by:

$$\text{Closed porosity} = \frac{\rho}{\text{Theoretical Density}}$$  \hspace{1cm} (25)

Samples are then taken out of the water and a swab is used to remove the surface layer of water and weighed again. This weight is used to determine the open porosity:
Vol open pores = \frac{\text{Mass}_{\text{wet}} - \text{Mass}_{\text{dry}}}{\rho_{\text{H}_2\text{O}}}

\text{Open porosity} = \frac{\text{Vol} \text{ OpenPores}}{(\text{Vol sample} + \text{Vol} \text{ OpenPores})}

Where Vol sample is calculated from Mass_{\text{dry}} and \rho.

### 4.5 Gelation Behavior

By adjusting the pH of the boehmite sol prior to the addition of CM and TEOS sol, sols gelling at different rates were obtained. The pH of boehmite sols were adjusted to 1.5, 2, 2.5, 3.5, 4.5, and 6 to create six SG samples and six SGCM samples. The viscosity of these sols was monitored over time using a Brookfield DV-E viscometer with spindle 3 at 100 rpm. All samples were stored covered at room temperature.

### 4.6 Glow Plugs

Two different glow plugs were used in this study, referred to as AA and BB glow plugs, shown in Figure 4-9. Both types of glow plugs were made of Si$_3$N$_4$ sintered with additive oxides, but have slightly different chemical compositions. Their chemical compositions were determined by EDX and are listed in Table 4-2. BB glow plugs, which are the ones currently used in DI-CNG engines for hot surface ignition, cost $65 each. Close to 100 plugs were used for this study. To reduce the cost of this study, the majority of the experiments were performed using AA glow plug, which were supplied by Westport Innovations, Inc. for free. AA glow plugs however were produced by a less recognized
manufacturer and were less reliable. Therefore, BB glow plugs were only used for the final development stages of the mullite coating.

Figure 4-9 AA glow plug (top) and BB glow plug (bottom)

<table>
<thead>
<tr>
<th>Glow plug</th>
<th>N</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>Y</th>
<th>Yb</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA</td>
<td>32</td>
<td>11</td>
<td>0.88</td>
<td>32</td>
<td>9.2</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>BB</td>
<td>38</td>
<td>4.9</td>
<td>0.31</td>
<td>48</td>
<td>3.2</td>
<td>1.7</td>
<td></td>
</tr>
</tbody>
</table>

Table 4-2 Elemental compositions of AA and BB glow plugs

A schematic of a glow plug is show in Figure 4-10. The hot ceramic tip extends out of the metal body which is fastened on into the engine block. The tip is made of sintered $\text{Si}_3\text{N}_4$ and embedded inside are two heating resistors containing electronically conducting tungsten carbide. One lead extends to the other end of the metal casing, and the other is connected to the grounded metal body. Powered by DC current, these glow plugs are capable of reaching temperatures of about 1400°C within few seconds. The hot spot of
the glow plugs, the point where the highest temperature is obtained, is typically at 3mm from the end of the glow plug. At ~5mm away from the hot spot, the temperature drops to ~1250°C. And at ~10mm away from the hot spot, the temperature drops to ~1000°C.

![Figure 4-10 Schematic of a glow plug](image)

### 4.7 Dip Coating Si$_3$N$_4$ Glow Plug Tips, Furnace Calcination

As this was a process oriented study, the process could not have been pre-determined. The method to determining the appropriate dip coating process was an iterative one. The process was refined step by step through the incorporation of results along the way. To begin, general dip coating processes were employed. As new insight into the process was acquired, modification to processing parameters such as viscosity and withdrawal speed were adjusted accordingly, until uniform and crack free coatings of different thicknesses were obtained.

Sols with selected viscosities were used to dip coat AA glow plugs. Since the body of the glow plug was not designed to withstand temperatures higher than 300°C, as it is composed of stainless steel, brazing and silicone parts which will not survive the heat treatment in the furnace, it was first necessary to detach the Si$_3$N$_4$ tips from the metallic
body. The tips were washed with distilled water and rinsed with ethanol prior to dip coating. The dipping was carried out using an in-house built dipper. Glow plug tips are held in a sample holder which is suspended by a cord. The cord is guided up and down by a pulley which is mounted to an electric motor.

![Diagram of dip coating process](image)

Figure 4-11 Diagram of dip coating process

The starting parameters were determined by estimation using the Landau and Levich equation, as described in Section 2.6:

\[
h = 0.94 \frac{(\eta \cdot V)^{2/3}}{\gamma_{LV}^{1/6} (\rho \cdot g)^{1/2}}
\]  

(27)
The values of liquid vapor surface tension $\gamma_{LV}$ and density $\rho$ were estimated to be similar to that of water which are 0.073 N/m and 1 g/cm$^3$ respectively. Samples were dip coated with a sol viscosity $\eta$ ranging from 10 cps to 80 cps and dipping speeds $v$ ranging from 0.1 mm/s to 5 mm/s. After dipping, tips were positioned vertically to air dry at room temperature. To prevent the formations of cracks from the solvent evaporating too quickly, the glow plug tips were shielded from air currents. The tips were left to dry for 12 hrs before calcination. As with calcination of the dried gel samples, the tips were calcined in a furnace with a heating rate of 8°C/min. Based on results of the calcination of dried gel samples, it was determined that mullitization should be complete after a heat treatment at 1300°C for 30 min. The coated tips were examined under the SEM to check for uniformity and thickness. Based on SEM results, the parameters were adjusted several times including using sols of different viscosity and changing dipping speeds, and using multiple dipping. Once uniform, dense and crack free coatings were achieved, calcination of the mullite coatings in situ was attempted.

### 4.8 Dip Coating Whole Glow Plugs, Calcination In-Situ

Usually, coating of Si$_3$N$_4$ objects require the whole part to be placed in a furnace or kiln for calcination. For the glow plugs, this was not possible as the non-ceramic components of the glow plug would not survive inside the furnace. However, since this was a unique circumstance where the substrate was capable of heat generation, it was possible to use itself for the calcination process. Intact glow plug samples were dip-coated using the most suitable viscosity and withdrawal speeds, which were previously determined on the detached glow plug tips calcined in the furnace. Glow plug temperatures were controlled
indirectly by control of applied DC voltage. Characterization of the heating curve of the glow plug, shown in Figure 4-12, determined that increasing power at a rate of 0.1V / 2min approximates a heating rate of approx 5°C / min. Beginning at 0.0 V, the voltage was increased at 0.1 V / 2min until approximately 14.0 V. The temperature of the glow plug was monitored using an optical pyrometer. When the tip temperature reached 1300°C, the voltage was sustained for 30 min. After calcination, the tips were examined under the SEM to check for uniformity and coating thickness.

![Figure 4-12 Heating curve of AA and BB glow plugs](image.png)

Later samples revealed that the dipping process described above was not able to produce a satisfactory coating. Down flow of the sol was causing a collection of excess sol near the tip, resulting in non uniform coatings which became heavily cracked or even missing
due to spallation. During the process of a simple dip coating, gravitation force is constantly acting in one direction, thus the film of sol, after being deposited onto the substrate, is constantly subjected to a downward pull. Before the film has fully gelled, the sol can flow downwards, creating a localized thick spot near the bottom. To avoid this, the dip and spin method was implemented. The dipping method was modified by putting the sample into constant rotation as it dried, and positioned horizontally instead of vertically, Figure 4-13. Being constantly reorientated, the effect of gravitational pull was not longer in one direction, avoiding the localized collection of sol. Furthermore, gravitational force now acted radially on the rotating glow plug; in combination with centripetal forces, they aided in producing an evenly distributed film of sol, resulting in a more uniform coating. Glow plug samples were washed with distilled water and rinsed with ethanol as was done previously. Dipping of the sample was done using the in house built dip coater. Immediately after dipping, samples were mounted horizontally and were continuously rotated at 600 rpm until it visually appeared to be dry (~5 min). The glow plugs were left to continue to air dry at room temperature and shielded from air currents for 12 hrs before calcination in situ.

![Figure 4-13 Horizontal orientation of glow plug while spinning @ 600 rpm after being dip coated](image)

Figure 4-13 Horizontal orientation of glow plug while spinning @ 600 rpm after being dip coated
4.9 Electric-Rig Testing

To evaluate the effectiveness of the coatings, two BB glow plugs were tested on an electric-rig. The electric-rig uses the same power supply as the one used for in-situ calcination. The glow plugs were mounted in an aluminum block to dissipate heat, as shown in Figure 4-14. One glow plug was coated while the other was tested in the as received state. Both glow plugs supplied with 15.5V DC current, operating at ~1300°C. After 100 hrs, the ceramic tips of both glow plugs were examined under the SEM for signs of degradation.

Figure 4-14 A BB glow plug mounted on the electric rig
5 Results and Discussion

5.1 Gelation Properties

The different sols prepared for studying the gelation properties are summarized in Table 5-1:

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>TEOS sol (ml)</th>
<th>AIOOH sol (ml)</th>
<th>CM (g)</th>
<th>AIOOH sol pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG1.5</td>
<td>11.6</td>
<td>100</td>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td>SG2.0</td>
<td>11.6</td>
<td>100</td>
<td>0</td>
<td>2.0</td>
</tr>
<tr>
<td>SG2.5</td>
<td>11.6</td>
<td>100</td>
<td>0</td>
<td>2.5</td>
</tr>
<tr>
<td>SG3.5</td>
<td>11.6</td>
<td>100</td>
<td>0</td>
<td>3.5</td>
</tr>
<tr>
<td>SG4.5</td>
<td>11.6</td>
<td>100</td>
<td>0</td>
<td>4.5</td>
</tr>
<tr>
<td>SG6.0</td>
<td>11.6</td>
<td>100</td>
<td>0</td>
<td>6.0</td>
</tr>
<tr>
<td>SGCM1.5</td>
<td>11.6</td>
<td>100</td>
<td>1.78</td>
<td>1.5</td>
</tr>
<tr>
<td>SGCM2.0</td>
<td>11.6</td>
<td>100</td>
<td>1.78</td>
<td>2.0</td>
</tr>
<tr>
<td>SGCM2.5</td>
<td>11.6</td>
<td>100</td>
<td>1.78</td>
<td>2.5</td>
</tr>
<tr>
<td>SGCM3.5</td>
<td>11.6</td>
<td>100</td>
<td>1.78</td>
<td>3.5</td>
</tr>
<tr>
<td>SGCM4.5</td>
<td>11.6</td>
<td>100</td>
<td>1.78</td>
<td>4.5</td>
</tr>
<tr>
<td>SGCM6.0</td>
<td>11.6</td>
<td>100</td>
<td>1.78</td>
<td>6.0</td>
</tr>
</tbody>
</table>

Table 5-1 Different sol samples and their compositions

The viscosity of the different prepared SG and SGCM sols were monitored over time. Results are shown in Figures 5.1 to 5.4. The viscosity of all 12 sols increased over time until complete gelation. The reason for this behavior was hydrolysis, as explained in Section 2.5.1. The pH of the boehmite sol affects the gelation speed. As can be seen in the viscosity vs time graphs, there is a quicker increase in viscosity as the pH of the sol decreased. The viscosities increased until they reached a maximum of ~ 80 cps for SG sols and ~140 cps for SGCM sols, at which point gelation is complete or is near complete. The degree of gelation for samples SG1.5, SG2.0, SGCM1.5 and SGCM2.0
increased so quickly that the sols were not usable in a practical sense (Figure 5-1 and Figure 5-3). Their viscosities at any given time changed within minutes, not allowing sufficient time for processing, making it impossible to obtain consistent coatings using these sols. Samples SG2.5 and SGCM2.5 gelled at a more manageable rate. Their viscosities remained steady over much longer durations allowing plenty of time for coating processing. Their viscosities increased by no more than 2 cps in 1 hr (Figure 5-2 and Figure 5-4). Samples SG3.5, SG4.5, SG6.0, SGCM3.5, SGCM4.5 and SGCM6.0 remained at low viscosities for much longer times. No significant increase in viscosity was detected until 24 hrs after preparation.
Figure 5-1 Viscosity change over time of SG1.5 and SG2.0 sols

Figure 5-2 Viscosity change over time of SG2.5, SG3.5, SG4.5 and SG6.0 sols

Lines added to increase readability of figures
Figure 5-3 Viscosity change over time of SGCM1.5 and SGCM2.0 sols

Figure 5-4 Viscosity change over time of SGCM2.5, SGCM3.5, SGCM4.5 and SGCM6.0 sols

Lines added to increase readability of figures
It appears contradictory that samples SG1.5, SG2.0, SGCM1.5, and SGCM2.0 were farther away from the isoelectric point, (where the zeta potential is zero and the double layer collapses, leading to flocculation of sol particles) but yet were more unstable resulting in quicker gelation. This phenomenon may be explained by the behavior of TEOS in acidic environments. Under acidic conditions, the hydrolysis of TEOS is acid catalyzed as follows [41]:

\[
\text{HOH} \quad \text{Si} \quad \text{OR} \quad \leftrightarrow \quad \text{Si} \quad \text{OR} \quad \text{OH} \quad \text{H}^+ \quad \text{OR} \quad \text{RO} \\
\]

(28)

Therefore, at higher acidity, there is an increased rate of hydrolysis and also a higher overall degree of hydrolysis, resulting in condensation more readily. Furthermore, the condensation process had been proposed to be acid catalyzed as well, by the following reactions [41]:

\[
\equiv \text{Si}^- \text{OH} + H_3O^+ \rightarrow \equiv \text{Si}^+ + 2H_2O \quad (29)
\]

\[
\equiv \text{Si}^+ + \text{HO}^- \text{Si} \rightarrow \equiv \text{Si}^- \text{O} = \text{Si}^- + H^+ \quad (30)
\]

Thus the higher gelation rates of samples SG1.5, SG2.0, SGCM1.5, and SGCM2.0 is likely the effect of acid catalyzed hydrolysis and condensation.

Sedimentation was noted in the SGCM sols. Into each batch of sol, 1.78g of CM was added, equating to 36wt% filler and 64wt% bulk in the final material. However, the
added CM settled out as the sols were left to age. After aging for 3 days, the settlement was separated from the sol and quantified. The settlement was dispersed into distilled water using an ultrasonic probe and subsequently filtered with a Fisher P2 filter. The amounts collected by the filters are plotted against corresponding pH of the boehmite sol, shown in Figure 5-5. The amount of CM sediment showed a correlation with the pH. At pH of 6, the amount of CM that settled out of solution was 61% of the added amount. This decrease reduces the final fraction of CM filler from 36% to about 18% (calculations in appendix). The amount of sediment decreased as pH decreases. At pH 2.5, 14% of the added amount settled out of the sol. This reduces the final fraction of CM filler from 36% to 32%. At a pH of 2.0 or less, however, gelation was complete before any significant amount of CM settlement. The stability of the mullite particles in suspension is governed by the zeta potential, which is influenced by acidity. These results follow a similar trend as the zeta potential curves measured in the study by [52] (refer to Figure 4-6). The zeta potential of mullite is well above 30mV at low pH, therefore the SGCM1.5 and SGCM2.0 samples showed little signs of sedimentation. As the pH increases above 4, zeta potential decreases, larger particles should begin to settle out of suspension. However, an increase in sediment amount was observed as pH increases above 2.5. This discrepancy maybe due to slight differences between particle size, or chemistry of powder used in this study and the study by Roncari et al. [52]. At pH 6, which is much closer to the IEP, less particles can remain in suspension, resulting in the majority of the CM addition settling out of suspension.
SGCM2.5 was chosen to be used for the coating stages of this work. A lower pH was selected to minimize the amount of CM settling out, balanced with a slower gelation rate allowing enough time for processing before gelation is reached.
5.2 Calcination

SG2.5 and SGCM2.5 sols were dried in crystallization dishes and calcined. Durations and temperatures of calcinations are summarized in the following table.

<table>
<thead>
<tr>
<th>Temp C</th>
<th>20 min</th>
<th>40 min</th>
<th>1hr</th>
<th>9hrs</th>
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</thead>
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<td>1200</td>
<td></td>
<td></td>
<td>●</td>
<td></td>
</tr>
<tr>
<td>1250</td>
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<td>1400</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
</tr>
</tbody>
</table>

Table 5-2 Calcination temperatures and durations

5.2.1 Phase Development vs Temperature

An essential step was to first check for mullite formation. It was necessary to confirm that the chosen sols resulted in the formation of mullite. The XRD results of gel cast samples confirmed the formation of mullite, Figure 5-6. Calcination of the SG sample at 1300°C for 1hr resulted in mullite as the main phase. The diffraction pattern showed clean peaks with little noise, suggesting that there was little amorphous region. The XRD pattern of the SGCM sample was very similar to the SG sample except trace amounts of corundum had also been identified. The corundum contained in the mullite amounts to 2.8wt%. It was suspected that the source of the corundum might have been the added CM. The XRD patterns of the as received CM sample showed the presence of cristobalite (1.8wt%) and corundum (9.4wt%), see Table 5-3 and Figure 4-8. Since the CM powder was not pure mullite, it could have been a source of corundum, and also cristobalite resulting in the any SGCM sample. However, formation of corundum during calcination was still a possibility. For the purpose of this project, presence of the
corundum will be considered negligible for two reasons. Firstly, even though a stoichiometric mix of precursors was used, perfect 3:2 mullite may not have been formed. Transitions to mullite of other Al$_2$O$_3$:SiO$_2$ ratios are also common [29]. If silica rich mullite is produced, it is possible that there would be residual alumina, existing in the form of corundum, and similarly if alumina rich mullite is produced, it is possible that there would be residual silica, existing in the form of cristobalite. Secondly, for the purpose of applying this coating is to protect the Si$_3$N$_4$ substrate, the presence of corundum will probably be beneficial to the ultimate purpose of the coating, since alumina has higher corrosion resistance than mullite. Therefore, the presence of the small amounts of corundum and cristobalite was regarded as negligible in this study.

![XRD patterns](image)

**Figure 5-6 XRD patterns of SG, and SGCM after calcination at 1300°C for 1hr.**
- mullite
After confirming the formation of mullite, the effects of calcination at different temperatures were examined. SG and SGCM samples were calcined for 1 hr at 1200°C, 1250°C, 1300°C, and 1400°C. The XRD patterns are shown in Figure 5-7. At 1400°C, the XRD pattern was not significantly different from the patterns given by the 1300°C samples other than trace amounts of cristobalite. It did not appear that calcinations at higher temperature had any significant effect. This indicated that calcination at 1300°C for 1 hr was sufficient to obtain mullite, and there was no benefit to calcination at temperatures above 1300°C. Decreasing in temperature however, showed a very interesting difference. The 1250°C SGCM XRD pattern closely resembles those patterns obtained at 1300°C and 1400°C. Equally narrow peaks and even back ground indicate

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mullite</th>
<th>Cristobalite</th>
<th>Corundum</th>
</tr>
</thead>
<tbody>
<tr>
<td>CM</td>
<td>88.8</td>
<td>1.8</td>
<td>9.4</td>
</tr>
<tr>
<td>1300 SGCM 9H</td>
<td>93.3</td>
<td>0.2</td>
<td>6.5</td>
</tr>
<tr>
<td>1300 SGCM 20m</td>
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<td>0</td>
<td>0.8</td>
</tr>
<tr>
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<td>99.2</td>
<td>0</td>
<td>0.8</td>
</tr>
<tr>
<td>1300 SG 9H</td>
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<td>4</td>
<td>0.2</td>
</tr>
<tr>
<td>1300 SGCM 1H</td>
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<td>0</td>
<td>2.8</td>
</tr>
<tr>
<td>1300 SG 20m</td>
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<td>0</td>
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<tr>
<td>1300 SG 40m</td>
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<td>0</td>
</tr>
<tr>
<td>1300 SG 1H</td>
<td>100</td>
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<td>0</td>
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<td>1250 SGCM 20m</td>
<td>92.2</td>
<td>4.7</td>
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<tr>
<td>1400 SG 1H</td>
<td>95.6</td>
<td>3.5</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Table 5-3 Phases of powder diffraction samples determined by Rietveld refinement
that the sample had a well developed mullite phase with little amorphous region. The 1250°C SG sample however, was completely different. The presences of the mullite peaks indicate that 1250°C was above the mullitization temperature, but the small size of the peaks suggest that mullite had only just begun to form. The other equally small but broader peaks were identified to be γ - alumina. It is a transitional phase that is form as boehmite decomposes at about 350°C [29]. This phase should be consumed during mullitization or corundum formation. The uneven background indicates that the sample was still mainly amorphous. Reducing the calcination to 1200°C appears to be below the mullitization temperature. The 1200°C SG sample showed no signs of mullite formation. The presence of small broad γ - alumina peaks only and a uneven background is indicative of a mainly fine grain or amorphous structure. The 1200°C diffraction SGCM pattern shows similar γ-alumina peaks and uneven background, with the addition of small narrow mullite peaks, likely from the 36wt% CM addition. This pattern indicates that the structure is mainly amorphous, containing γ - alumina which had yet to be consumed because mullite formation had not commenced, with CM mullite dispersed yielding the narrow mullite peaks.
5.2.2 Phase Development vs Time

The effect of calcination time was also investigated. Diffraction patterns of samples calcined at 1300°C for 20min, 40min, and 1hr are shown in Figure 5-8. All the patterns were very similar, indicating that the majority of reactions had already taken place and mullitization had reached near completion after only 20 min at temperature. To check the effects of being at elevated temperatures for prolonged durations, samples were calcined for 9hrs at 1300°C and 1400°C. Cristobalite was detected in all four samples, shown in Figure 5-9. The cristobalite is likely to have formed from residual amorphous silica, given the long duration, and unlikely to have formed from the decomposition of mullite. However, the cristobalite makes up only 4wt% of the sample or less. As mentioned previously, the little amounts that have been detected are regarded as tolerable for the purpose of this project. In the samples calcined at 1250°C, the effect of time was more
apparent. As can be seen in Figure 5-10, after 40 min of calcination of the SG sample, mullite phase is not detected. Only small amounts were detected after 1 hr. Judging from the small size of the peaks, the amount of mullite formation is estimated to be ~10 wt%. From the XRD spectrum of the SGCM samples, however, it is clearly evident that after 20 min, there had already been a significant amount of mullite formation with small amounts of γ-alumina remaining unreacted. After 40 min, mullite formation was near completion.

**Figure 5-8** XRD patterns after calcination at 1300°C for different times

- mullite
5.2.3 Effect of CM Addition on Phase Development

Samples with the mullite addition showed an earlier completion of mullitization. The 1250°C SGCM 1hr sample showed a significantly higher degree of mullitization than the 1250°C SG 1hr sample. SGCM was near completion while only ~10wt% was detected in the SG sample. Both being calcined for the same duration of 1hr, this comparison confirms that the addition of CM allowed mullite formation to complete more quickly.
By comparing the 1hr diffraction patterns (Figure 5-7) of the 1200°C SGCM sample and the 1250°C SGCM, it can be confirmed that the mullite peaks in the pattern given by the 1250°C SGCM sample was not only from the CM content, but from newly formed mullite as well. Mullite peaks from 1250°C SGCM are comparably larger than from 1200°C SG. The difference should therefore be the result of newly formed mullite, because the CM alone should yield only small peaks which resemble those in the 1200°C SGCM sample. The lack of γ-alumina peaks is also indicative of mullite formation as γ-alumina is completely reacted during mullite formation. The effect of CM addition is further demonstrated (Figure 5-10) where the SGCM sample had reached almost complete mullitization after only 40 min at 1250°C, while the SG sample required 1hr to begin.

The above evidence demonstrates that the addition of CM encourages the formation of mullite. The seeding effect of increased kinetics as described for alumina by Kumagai and Messing [48] was also observed here for mullite. The dispersed CM particles acted as seeds, providing sites for crystallization and encouraging earlier mullite formation [49]. Normally, formation of mullite involves a nucleation step where the nucleation density of $2 \times 10^{11} \text{ cm}^{-3}$ is reached before grain growth [29]. The addition of CM has shorted this stage. However, the effect of the addition of CM on mullitization temperature is unclear. It was difficult to determine whether the 1200°C SGCM sample contained small amounts of newly formed mullite which is masked by the CM. It has been reported that formation of mullite at 1200°C is possible [53]. It can only be concluded that even if mullite has already begun to form, the formation was only to a
undetectable extent. Thus, the realizable effect of CM addition seems to be limited to reducing calcination times.

5.3 Characterization of SG and SGCM Mullite

TGA results for both types of samples are show in Figure 5-11. Much of the weight lost occurs below 500°C. The first major drop at <200°C corresponds to final solvent evaporation. This accounts for the over 50% of the total weight loss in both samples. The next drop at around 350°C corresponds to burning out of organics and the dehydroxylation of boehmite forming gamma/delta alumina. The original curve of the SGCM sample showed a smaller weight loss than the SG sample. This reduced weight loss is a good sign that the addition of the CM filler lead to a reduction to shrinkage. However, when the weight loss is adjusted for the fraction of CM (which is fully calcined and should have no mass loss and shrinkage upon processing), the mass loss becomes very comparable. This result suggests that the heating rate during calcinations is more critical below 500°C. The heating rate should be low to allow enough time for the solvent (and organics) to leave the system slowly, to minimize stresses that may build up during shrinkage. Above 500°C, the material should be less sensitive to heating rates.
The fracture surface of the calcined SG sample, shown in Figure 5.11, appears to be dense and free of voids. The density of the calcined SG sample was determined to be 3.11 g/cm$^3$, which is lower than the theoretical mullite density of 3.17 g/cm$^3$. Figure 5.13 lists average compositions of calcined SG and SGCM samples. When looking at the average elemental content measured using EDX, it can be seen that the Al:Si ratio is 2.5, which is lower than the theoretical ratio of stoichiometric mullite (as mentioned in Section 4.3, the Al:Si wt% ratio is compared to the stoichiometric ratio of 2.88). The higher Si content indicates that the mullite is either a silica rich mullite, or contains excess silica in the form of glassy phases. It is not silica in the form of cristobalite because none was detected in the XRD analysis. Closed and open porosity were determined to be 1.8% and 1.1% totaling to 2.9%. It is known that porosity affects
material properties such as elastic modulus and strength [29]. The elastic modulus is correlated to porosity by the formula:

\[ E = E_0 (1 - bP) \]  

(31)

Where \( b \) is a constant and is determined to be 3.8 for mullite [29]. At a porosity of 2.9%, the elastic modulus of the SG sample is estimated at 204 GPa, which is 89% of theoretical.

Examination of a fractured surface of the SGCM sample under the SEM revealed that it was not as smooth as the SG sample, Figure 5-12. Undesirably, the bulk mullite from SG and the CM did not completely amalgamate into one homogeneous material. Particles of the dispersed CM can easily be identified in the SEM micrograph. Judging by comparing to the micrograph of the as received CM powder, these particles appear to be either the larger particles in the CM powder, or agglomerates of smaller particles which were not completely broken up and dispersed during ultrasonication. Judging form the material surrounding the particles, however, it appears that the smaller particles might have melded into one uniform material, as predicted. The fracture surface is relatively smooth, and is only interrupted by the larger particles. This suggests that aside from the large chunks this has become a homogenous mullite. Elemental constituent measurements show a Al:Si ratio of 3:19, Table 5-4, indicating that the mullite maybe alumina rich. The CM content which has a ratio of 3.30 may have also contributed to the higher reading. The higher amount of Al in the as received powder, is reflected in the XRD
results as small corundum peaks. As mentioned previously, although unintended, the corundum is likely to be beneficial for the purpose of an EBC. The density of the calcined SGCM samples was determined to be 3.01 g/cm$^3$. The closed and open porosity were determined to be 5.0% and 4.4% respectively, totaling 9.4%. At 9.4% porosity, the estimate of elastic modulus of the SGCM material reduces to 147 GPA, 60% of theoretical. However, the lower elastic modulus of the SGCM sample may be beneficial in the application of coatings on Si$_3$N$_4$ because thermal stresses are reduced. The thermal stress for very fast heating and cooling can be estimated (neglecting system geometry and Poisson’s ratio effects) by equation:

$$\sigma = E \cdot \Delta \alpha \cdot \Delta T$$

(32)

The CTE of mullite is $\sim 6 \times 10^{-6}$ /°C compared to $3.3 \times 10^{-6}$ /°C of Si$_3$N$_4$, thus $\Delta \alpha = 2.7 \times 10^{-6}$ /°C. $\Delta T$ is 1300 for operations at 1300°C. Using the values of $E$ determined above, thermal stresses which will develop in a SG coating and a SGCM coating could be 716 MPa and 515 MPa respectively. This amount of stress is likely greater than the strength of the coatings and will thus result in cracking.
Figure 5-12 Micrographs of fracture surface of calcined SG and SGCM bulk samples
Table 5-4 Average compositions of heat treated samples

<table>
<thead>
<tr>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>Al:Si ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SG calcined gel cast</td>
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<td>30</td>
<td>13</td>
</tr>
<tr>
<td>SGCM calcined gel cast</td>
<td>52</td>
<td>36</td>
<td>11</td>
</tr>
<tr>
<td>CM only</td>
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<td>34</td>
<td>10</td>
</tr>
<tr>
<td>3:2 Mullite theoretical values</td>
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<td>13</td>
</tr>
<tr>
<td>2:1 Mullite theoretical values</td>
<td>30</td>
<td>25</td>
<td>6.6</td>
</tr>
</tbody>
</table>

5.4 Dip Coating Si$_3$N$_4$ Glow Plug Tips, Heat Treatment in Furnace

The initial targeted coating thickness was ~3µm. Factoring in shrinkage, the wet film coating was required to be ~80 µm thick. From dried gel samples, the volume of the dried SGCM gel was measured to be 3% of the sol, thus a wet film of 80 µm thick should dry to 2.4µm thick. Using the Landau and Levich equation, the possible parameters for sol viscosity and the dipping speed were calculated to be 80 cps and 5 mm/s respectively. Tip1 is shown in Figure 5-13, with a coating of thickness of ~6 µm. This value is more than twice the estimated thickness. This discrepancy may have resulted from the inaccurate estimates of surface tension and density of the sol. Another source for discrepancy is in the measurement of viscosity. As sols are non-Newtonian fluids, the viscosity is dependent on strain rate. The dipping speeds used were different from the speed of the viscometer used to monitor the sols. However, since the values are within the same order of magnitude, it still gave a good starting point. At a thickness of 6 µm, the coating is severely cracked and spallation was evident.
Figure 5-13 Tip1 (80 cps, 5mm/s) Spallation and extreme cracking of coating

To obtain a thinner coating on Tip2, the sol was used at a viscosity of 50 cps, at the same dipping velocity of 5 mm/s. The calcined coating, which was now ~5µm thick, remained to be cracked, as shown in Figure 5-14.

Figure 5-14 Tip2 (50cps, 5mm/s) Severe cracking of coating. Spallation also evident.

As the previous coatings were too thick to be crack free, the next approach was to produce a much thinner coating; rather thin but crack free. Again, the SGCM2.5 sol was used, but at the viscosity of 10 cps. The withdrawal speed remained at 5 mm/s. The resulting coating on Tip3 is show in Figure 5-15. At this viscosity a new issue came about. A droplet of sol collected at the tip of the glow plug, forming a very localized spot of very thick coating, which flaked off when dried. Because the viscosity of the sol was
so low, the wet film exhibits down flow before the coating gelled. The wet film was partially forced down by gravitational pull, creating a drop collecting at the tip.

![Image](image.jpg)

**Figure 5-15 Tip3 (10cps, 5mm/s) End of tip is bare caused by drip formation which flaked off after drying**

This required the withdrawal speed to be lowered. Reduction of the withdrawal speed deposits a thinner film onto the substrate and allowed more time for excess sol to flow back into the sol before the tip was completely withdrawn. The withdrawal speed was lowered gradually, but even at a speed of 0.1mm/s, which was the slowest setting on the dip coater, down flow was still evident. Tip4 is shown in Figure 5-16. Aside from the drip collected near the tip, the glow plug tip was uniformly coated with a very thin coating, estimated to be $< 0.5\mu$m.
Figure 5-16 Tip4 (10cps, 0.1mm/s) Tip end partially bare due to flaking of dried coating. Substrate can be seen through the coating.

To increase the thickness and to reduce the amount of down flow, a higher viscosity was used. Dipping was done when the SGCM2.5 sol has aged until it had reached a viscosity of 30 cps and dipping speed at remained at 0.1mm/s. At this setting, a collection of a drop near the tip is no longer noticeable after drying. It only became apparent after calcination that a slight amount of collection still occurred, however, much smaller than previous samples. Tip5 is shown in Figure 5-17, the calcined coating had good uniform coverage. Cracking was still evident, and from these cracks, the thickness of the coating was estimated to be ~1µm.

Figure 5-17 Tip5 (30cps, 0.1mm/s) Less spallation near end of tip. Uniform coating with minimal cracking
To compensate for the lower coating thickness, multiple dipping was used. Figure 5.19 shows a Tip6 which was dipped and dried twice in a SGCM2.5 sol, increased to 40 cps, but also at 0.1mm/s to produce a coating that was twice as thick. The calcined tip had a much reduced amount of localized collection of sol near the tip. This coating was 3µm thick, coverage was uniform and significantly fewer cracks were found. Although not completely defect free, these dipping parameters were implemented in the next stages of the experiments: coating intact glow plugs and calcining in situ. Further refining of dipping parameters was carried out at a later stage. Table 5-5 summarizes the above results.

Figure 5-18 Tip6 (40cps, 0.1mm/s, 2x) No spallation of coating and almost crack free.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Dip Coating Parameters</th>
<th>Coating thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>η (cps)</td>
<td>ν (mm/s)</td>
</tr>
<tr>
<td>Tip1</td>
<td>80</td>
<td>5</td>
</tr>
<tr>
<td>Tip2</td>
<td>50</td>
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</tr>
<tr>
<td>Tip6</td>
<td>40</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 5-5 Summary of coated samples and the dip coating parameters used
5.5 Dip Coating Whole Glow Plugs, In-Situ Heat Treatment

Using the same processing parameters as Tip6 (40 cps sol, 0.1 mm/s withdrawal speed, dip 2x), which worked best for the detached AA glow plug tips, intact AA glow plugs were coated and heat treated in situ. The results are shown in Figure 5-19. Uniformity of the coating was comparable to the coating on the detached tip, demonstrating reproducibly. The streak seen in the micrograph is from a primitive scratch test done by scraping the sample with a scalpel. The coating in the region closer to the metallic body, which operates at much lower temperatures, was completely scraped off. This region of the glow plug operates at around 1000°C and thus, the coating never reached the required temperature, 1250°C, resulting in a coating with properties near to that of dried gel. Closer to the tip, in the region of the hot spot, the coating was not removed by the stroke of the scalpel. But rather, residue of the metal blade was left behind on the surface of the coating, showing that the hardness of the coating is greater than that of the scalpel blade, and that the coating is well adhered to the surface of the glow plug. This is a good indication (although entirely qualitative) that the coating covering this hot region was well sintered, demonstrating that heat treatment directly on the glow plug tip is achievable with good coating coverage and adhesion.
Figure 5-19 An AA glow plug calcined in situ. Scalpel scratch direction towards top of page.

Top: hotter region, scalpel residue left on coating (>1250 °C)
Bottom: cooler region, coating removed by scalpel (<1000 °C)

The presence of the dimpled and blistered texture, however, introduced a new concern.
This was first noticed in the samples which were calcined in the furnace. From various
locations of the glow plug tip, evidence of different stages of dimples and blister formation could be found, as shown in Figure 5-20. Initially small bumps began to form. The bumps then bubble up from gas evolution from underneath the coating. The bubbles eventually burst, leaving a dimpled and blistered texture.

![Figure 5-20 Various degrees of bumpy and blistered texture found in coating after calcination](image)

To determine at what point during processing the dimples and blisters were actually formed, the coating was examined under the SEM at different stages of the calcination process. The results are shown in Figure 5-21. During ramping, the coating stayed smooth and intact, at 6V, at 11V, at 15V (~1250°C). There were no signs of blisters until
after the ½ hr hold at 15.4V (~1300°C). From this exercise, it can be concluded that the blisters are not a result of final drying of the solvent or decomposition of boehmite to γ-alumina, which occurs at about 100°C and 350°C respectively (refer to the results from earlier section, Figure 5-11). The blisters were formed during the hold at 1300°C. It is speculated that this could be caused by a reaction between the coating and the AA glow plug material, such as residual carbon reacting with SiO₂, forming CO and SiO gas. Fortunately, it was later found out that coated BB glow plugs did not exhibit the dimpled and blistered texture. Further investigation into the cause was put aside for future study. However, it was beneficial to learn that the final drying of the gel and decomposition of boehmite does not result in cracking, which had also been a big concern.

Figure 5-21 Texture of coating at various stages of ramping
Even though GP tips were overall well coated, the droplet near the tip remained to be a concern. The hot spots of glow plugs are usually near the very tip, and so it is at the tip where degradation is most severe and protection is most needed. Collection of this droplet happens to be right at the tip of the glow plug due to the vertical orientation of the glow plug during processing. As a result, when the droplet cracks and flakes off, the part of the glow plug which needs the protection the most becomes exposed. As a countermeasure, the approach of coating by dipping and spinning was implemented. Glow Plugs were coated by dipping and spinning as described in Section 4.8. In the low magnification photo, Figure 5-23, it can be seen that the collection of the drop is no longer apparent.

![Image](image.png)

**Figure 5-22** Comparison of glow plugs coated by dipping vs dipping and spinning. Collection near end of tip is evident on glow plug coated by dipping only

The coatings that were calcined using the BB glow plug are shown in Figure 5-23 and 5-24. Dip and spin coating was used for all BB glow plugs. Both SG and SGCM coatings were uniform, without the dimpled and blistered texture. In the glow plug coated with SG, the coating was estimated to be 2.5µm thick while the glow plug coated with SGCM
had a coating estimated to be slightly thicker, around 3 µm. The difference between coating with SG and coating with SGCM could be immediately noted. The SG coating exhibited circumferential cracks. These cracks, around 1.5 µm wide, are believed to be caused by post-sintering shrinkage. Due to the cylindrical geometry of the glow plug, a small change in dimension circumferentially translates to a much greater change lengthwise. So it is no surprise that the cracks were predominately circumferential, like a series of ring along the length of the glow plug tip. They can be seen in the low magnification photo of Figure 5-23. Over the 4mm hot spot region of the glow plug, the series of cracks were found to be 2-3 µm wide, producing a total opening of ~18 µm. This is close to the expected amount of cracking which is estimated by:

\[ \Delta L = \Delta \alpha \Delta T \times 4000 \, \mu \text{m} \quad (\Delta \alpha = 2.7 \times 10^{-6} / ^\circ \text{C} , \Delta T = 1300 ^\circ \text{C}) \] (33)

\[ \Delta L = 14 \, \mu \text{m} \]
These regular circumferential cracks were not found in the SGCM coated glow plugs. However, a different type of cracks was found in the SGCM coating, Figure 5-24. These irregular cracks had the shape of an opened slit and appear to originate at from a large chunk of calcined mullite, 2-3 µm large. These chunks could be found throughout as can be seen in the other figures of SGCM coatings and also in the bulk samples shown in Figure 5-12. These chunks resemble the particles found in the as received CM powder shown in Figure 4-7. Considering the similar EDX analysis results (refer to Table 5-6), these chunks should have originated from the CM powder. They are either larger sized particles, or agglomerates of the powder that did not get broken up during processing. As
the coating was dried and calcined, the presence of these chunks became weak spots and failed in tension as drying stresses increased. Densification shrinkage and differential cooling shrinkage continued opening these cracks. If a finer powder had been used, it is probable that the SGCM coating would exhibit less cracking. Aside from the cracks, the coating appeared similar to the calcined bulk material (Figure 5-12). The texture and roughness were comparable. Furthermore, the elemental constituents obtained from EDX were also comparable. The similar Al:Si wt% ratio suggest that they have the same phase constituents. Combining the results from SEM and EDX analysis, it is convincing that the SGCM mullite coating produced on the GP tip is similar to SGCM mullite in bulk and should have similar properties as well.

Figure 5-24 BB glow plug with SGCM coating. Coating is uniform but small slit cracks are evident.
<table>
<thead>
<tr>
<th></th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>Yb</th>
<th>Al:Si ratio</th>
</tr>
</thead>
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<tr>
<td>SG coating on BB glow plug</td>
<td>53</td>
<td>29</td>
<td>15</td>
<td>2.5</td>
<td>1.9</td>
</tr>
<tr>
<td>SGCM coating on BB glow plug</td>
<td>57</td>
<td>32</td>
<td>10</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>chunks in SGCM coating</td>
<td>59</td>
<td>31</td>
<td>9.6</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>SG calcined gel cast</td>
<td>57</td>
<td>30</td>
<td>13</td>
<td>2.3</td>
<td></td>
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<tr>
<td>SGCM calcined gel cast</td>
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<td>36</td>
<td>11</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>CM only</td>
<td>55</td>
<td>34</td>
<td>10</td>
<td>3.3</td>
<td></td>
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<tr>
<td>3:2 Mullite theoretical values</td>
<td>49</td>
<td>38</td>
<td>13</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>2:1 Mullite theoretical values</td>
<td>30</td>
<td>25</td>
<td>6.6</td>
<td>3.8</td>
<td></td>
</tr>
</tbody>
</table>

Table 5-6 Average compositions of coatings heat treated in-situ

5.6 Electrical Rig Testing of Coated Glow Plug

An as-received BB glow plug and a SGCM coated BB glow plug were tested on an electrical rig for 100hrs at a voltage of 15.5V. As can be seen in Figure 5-25 and 5-26, the surface of the as-received glow plug had developed a distinct surface layer. EDX analysis of this layer showed a high amount of Yb content, suggesting that the substance was Yb$_2$Si$_2$O$_7$. This layer of Yb$_2$Si$_2$O$_7$ was formed by Yb$^{3+}$ ions which had diffused outwards from the bulk material and had reacted with the SiO$_2$ and O$_2$, as confirmed in recent publication [25]. Examination of the cross section at the hot spot reveals that this Yb$_2$Si$_2$O$_7$ layer is ~2 µm thick. When examining the surface of the coated BB glow plug, shown in Figure 5-26, the glow plug appeared to be well cover by the mullite coating. Some cracking is apparent, similar to the cracks that were observed in the SGCM coating in the previous section. Presence of Yb$_2$Si$_2$O$_7$ was not evident except in the vicinity of cracks. Examination of the cross section at the hot spot revealed that the mullite coating was dense and had a thickness of ~1.5µm. Under the mullite coating, a layer of Yb$_2$Si$_2$O$_7$
had also developed. However, compared to the as-received glow plug, this layer was much thinner, with a thickness of approximately 0.5 µm.

Figure 5-25 Micrographs of surface and cross section of as received BB glow plug after 100hrs on electric rig
Figure 5-26 Micrographs of surface and cross section of SGCM coated BB glow plug after 100hrs on electric rig

Much less Yb$_2$Si$_2$O$_7$ formed in the coated glow plug. The layer of Yb$_2$Si$_2$O$_7$ that had formed was only a quarter of that of the as-received glow plug. It appears that the mullite layer provided a barrier against inward oxygen diffusion, which reduced the penetration of oxygen into and oxidation of the bulk Si$_3$N$_4$ material to SiO$_2$. Without the increased
grain boundary phase, Yb$^{3+}$ diffuses outwards less readily, resulting in the formation of a thinner Yb$_2$Si$_2$O$_7$ layer. Although the oxidation process on the electric rig took place in air, this comparison between the coated and uncoated glow plug clearly shows that the oxidation of the Si$_3$N$_4$ substrate is significantly reduced by the mullite coating. With a reduced oxidation rate, it looks promising that the mullite coating will offer some protection in a combustion environment as well.
6 Conclusion

In combustion environment such as in the hot gas paths of turbines, or inside direct injection compressed natural gas (DI-CNG) engines, silicon nitride $\text{Si}_3\text{N}_4$ is susceptible to paralinear oxidation. Oxygen and water in such environments oxidize $\text{Si}_3\text{N}_4$ forming a silica layer. Concurrently, water and carbon monoxide can react with this oxide layer forming volatile hydroxides. Through this process of oxidation and volatilization, $\text{Si}_3\text{N}_4$ can become significantly corroded. The addition of rare earth oxides as sintering aids in $\text{Si}_3\text{N}_4$ adds to the severity of the situation by increasing the volume of the grain boundary phases and increasing rates of diffusion. Glow plugs made of $\text{Si}_3\text{N}_4$ operating in DI-CNG engines fail after 1000hrs of service due to degradation and loss of material. To protect $\text{Si}_3\text{N}_4$ Glow Plugs from such harsh environments, mullite environmental barrier coating (EBC) has been investigated in the present work. Mullite has high corrosion resistance, good high temperature strength, and its coefficient of thermal expansion $\text{CTE}=4.5-6 \times 10^{-6}/\degree\text{C}$, is a relatively close to that of $\text{Si}_3\text{N}_4$ ($\text{CTE}=3.3 \times 10^{-6}/\degree\text{C}$). In this study, it was proposed that a mullite-mullite EBC for $\text{Si}_3\text{N}_4$ be applied by the novel composite sol gel process. The addition of calcined mullite (CM) powder in the sol should reduce the overall shrinkage of a sol, making the deposition of thicker coatings (>1µm) possible.

Sol gel mullite precursors were prepared combining TEOS sol with AlOOH sol. Commercially available calcined mullite was dispersed in the sol, with a solid loading of up to 36%. Gelation of these sols were studied and it was found that preparation of such sols using AlOOH sols at a pH of 2.5 gave the best balance of gelation rate and calcined mullite sediment rate. This formulation was the most suitable for use in dip coating
because it had a wide window for processing without sacrificing much CM loading through sedimentation.

When samples were calcined, it was determined that heat treatment of SG samples at 1300°C for 20min was required to achieve near complete mullitization. However, the addition of CM allowed the composite SGCM samples to obtain a similar extent of mullitization at 1250°C. It was hypothesized that the addition of CM into the sol acted as seeds, reducing the nucleation step during mullite formation. This is beneficial to the applications, such Si₃N₄ glow plugs, as calcination in situ is possible without pushing the operation limits of the glow plug much beyond the nominal 12V DC.

Calcined SGCM samples had a density of 3.01g/cm³, with a total porosity of 9.4%. At this amount of porosity, the elastic modulus is expected to be reduced to about 60% of the theoretical value for fully dense mullite. This lower stiffness of the coating may also be beneficial in the application of EBCs for Si₃N₄, as it proportionally reduces the amount of thermal stresses during operation.

Depositing the coatings on glow plug tips proved to be most difficult. After many trials, dip coating two times using SGCM sol of 40 cps viscosity and a dipping speed of 0.1mm/s provided the most desirable results. Relatively crack free coatings of ~3µm could be produced in such operation. SG coatings of lower thickness exhibited a greater amount of cracking, demonstrating that the addition of calcined mullite indeed reduced the amount shrinkage during processing. However, even though processing shrinkage
was reduced, it remained difficult to produce entirely crack free EBC as the CTE of mullite and Si₃N₄ still differ by a factor of 1.4-2.

Testing of the glow plugs on the electric rig proved effectiveness of the mullite EBC. Oxidation of the Si₃N₄ substrate was significantly reduced. The coating effectively limited oxygen diffusion, resulting in a reduction in thickness of the Yb₂Si₂O₇ corrosion layer formed. After 100hrs at 1300 °C, the layer of Yb₂Si₂O₇ found in the coated glow plug was only ¼ of that of the as received glow plug. Although not tested in a combustion environment, the performance of this mullite-mullite environment barrier coating appears to be promising.
7 Recommended Future Work

In this work, mullite-mullite environmental barrier coatings ~3μm thick were deposited on Si₃N₄ substrates by composite sol gel. Current results are promising and investigations into this process should continue. Although coatings ~3μm thick were obtained, and have shown significantly less cracking, they were not crack free. Greater CM loading may further reduce cracking due to processing and allow for even thicker coatings to be deposited. The electric rig testing showed positive results in terms of oxidation protection, but only one pair of glow plugs were examined. A greater number of glow plugs should be tested to increase statistical significance of the results. Furthermore, the testing was only carried out for 100hrs. It would be beneficial to repeat the test for a longer duration to provide insights into whether durability of coated glow plugs would be improved. Other aspects of the coating should also be examined, such as the effects of thermal shock and thermal cycling. In the intended application of the glow plugs in DI-CNG engines, operating temperatures fluctuate more than 1000°C with every stroke of the piston. To more accurately test the performance of the coatings, testing should be carried out in a combustion atmosphere. It is recommended that further evaluation be performed in a burner rig and subsequently an engine rig to better simulate conditions during operations. Finally, the current application in natural gas engines resulted from the movement towards alternative fuels. It would be beneficial to also perform burner rig and engine rig testing using other fuels, including H₂-CNG mix and H₂ gas, to explore further possible applications of mullite-mullite environmental barrier coatings when using other alternative fuels.


8 References


[2] Private communication from Alan Welch and Colin Blair, Westport Innovations Inc


Calculations for CM loading

In 11.2 ml of TEOS (Si(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4} sol (density = 0.933 g/ml, molecular weight = 208.32 g/mol),

\[
11.2 \text{ ml} \times 0.933 \text{ g/ml} \div 208.32 \text{ g/mol} = 0.050 \text{ mol TEOS}
\]

there was 0.05 mol TEOS, potentially forming 0.05 mol of SiO\textsubscript{2}. At a ratio of 3:2 for stoichiometric mullite (3Al\textsubscript{2}O\textsubscript{3}·2SiO\textsubscript{2}),

\[
0.05 \text{ mol} \times \frac{3}{2} = 0.075 \text{ mol}
\]

0.075 mol of Al\textsubscript{2}O\textsubscript{3} is required. Since 2 mols of AlOOH is required to form 1 mol of Al\textsubscript{2}O\textsubscript{3},

\[
0.075 \text{ mol} \times 2 = 0.15 \text{ mol}
\]

0.15 mol of AlOOH is required. This was obtained from 300ml of 0.5M AlOOH sol.

From 0.05 mol of TEOS and 0.15 mol of AlOOH, 0.025 mol of SG mullite should be formed. With a molecular weight of 384.17 g/mol,

\[
0.025 \text{ mol} \times 384.17 \text{ g/mol} = 9.60 \text{ g}
\]

9.60 g of SG mullite was produced in one batch. Each batch was divided into 3 for the preparation of 3 samples,

\[
9.60 \text{ g} \div 3 = 3.20 \text{ g}
\]

thus in each sample, there was 3.20 g of SG mullite

For SGCM samples, 1.78 g of CM was added to each sample.

\[
\frac{1.78 \text{ g}}{3.20 \text{ g} + 1.78 \text{ g}} = 36\%
\]

Therefore, each SGCM contains 36% CM.
Calculations for CM loading after sedimentation

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<tr>
<th>pH</th>
<th>1.5</th>
<th>2.0</th>
<th>2.5</th>
<th>3.5</th>
<th>4.5</th>
<th>6.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>settle out (g)</td>
<td>0.01</td>
<td>0.01</td>
<td>0.256</td>
<td>0.755</td>
<td>0.942</td>
<td>1.09</td>
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<td>added amount (g)</td>
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<td>1.78</td>
<td>1.78</td>
<td>1.78</td>
<td>1.78</td>
<td>1.78</td>
</tr>
<tr>
<td>% of added</td>
<td>0.56%</td>
<td>0.56%</td>
<td>14.38%</td>
<td>42.42%</td>
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<td>Mullite from SG (g)</td>
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<td>3.20</td>
<td>3.20</td>
<td>3.20</td>
<td>3.20</td>
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<tr>
<td>still suspended (g)</td>
<td>1.77</td>
<td>1.77</td>
<td>1.524</td>
<td>1.025</td>
<td>0.838</td>
<td>0.69</td>
</tr>
<tr>
<td>Final % CM loading</td>
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<td>35.60%</td>
<td>32.25%</td>
<td>24.25%</td>
<td>20.75%</td>
<td>17.73%</td>
</tr>
</tbody>
</table>

Sample calculation for pH 2.5

CM added = 1.78g
Settle out = -0.256g
Remaining in suspension = 1.52g

Final CM loading is

\[
\frac{1.25g}{3.20g + 1.25g} = 32.25\%
\]
Calculations for initial dip coating parameters

Landau and Levich equation predicts the coating thickness \( h \),

\[
h = 0.94 \frac{(\eta \cdot \nu)^{2/3}}{\gamma^{1/6} (\rho \cdot g)^{1/2}}
\]

\( \eta = \text{input 80 cps, 0.080 Ns/m}^3 \)
\( \nu = \text{input 5 mm/s, 0.005 m/s} \)
\( \gamma = \text{assume 0.0728 N/m} \)
\( g = 9.8 \text{ m/s}^2 \)
\( \rho = 1000 \text{ kg/m}^3 \)

\[
h = 0.94 \frac{(0.080 \cdot 0.005)^{2/3}}{(0.0728)^{1/6} (9.8 \cdot 1000)^{1/2}} \frac{\left( \frac{Ns}{m^2 \cdot s} \right)^{2/5}}{\left( \frac{Ns}{m^2 \cdot s} \right)^{1/6} \left( \frac{m}{kg} \right)^{1/2}}
\]

\[ h = 79 \times 10^{-6} \text{ m, 79 } \mu \text{m} \]

coating dries to 3% of thickness

\[ 79 \mu \text{m} \times 3\% = 2.39 \mu \text{m} \]
### Calculation for density and porosity of SG and SGCM samples given in section 5.3

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<thead>
<tr>
<th></th>
<th>SG</th>
<th>SGCM</th>
</tr>
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<tbody>
<tr>
<td>pycnometer</td>
<td>16.86 g</td>
<td>pycnometer</td>
</tr>
<tr>
<td>pycnometer + SG</td>
<td>19.562 g</td>
<td>pycnometer + SGCM</td>
</tr>
<tr>
<td>pycnometer + SG + H2O</td>
<td>43.751 g</td>
<td>pycnometer + SGCM + H2O</td>
</tr>
<tr>
<td>H2O mass</td>
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<td>H2O mass</td>
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<tr>
<td>H2O vol</td>
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<td>0.86795 ml</td>
<td>SGCM vol</td>
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<td>mass of H2O in pores</td>
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<td>density SG from above</td>
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<td>density SGCM from above</td>
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<tr>
<td>vol SG</td>
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</tr>
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<td>vol H2O</td>
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<tr>
<td>total porosity SG</td>
<td>2.91 %</td>
<td>total porosity SGCM</td>
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</table>

*denotes H2O density measured to be 1.00236 g/ml