CMZP and Mg-doped Al₂TiO₅ Thin Film Coatings for High Temperature Corrosion Protection of Si₃N₄ Heat Exchangers

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(ABSTRACT)

Silicon nitride (Si_3N_4) is a potentially good ceramic material for industrial heat exchangers. However, at elevated temperatures and in coal combustion atmospheres its lifetime is severely reduced by oxidation. To increase its corrosion resistance, the formation of a protective oxidation barrier layer was promoted by the deposition of oxide thin films. Homogeneous and crack-free oxide coatings of calcium magnesium zirconium phosphate (CMZP) and magnesium doped aluminum titanate (Mg-doped Al₂TiO₅) were successfully deposited on Si_3N_4 using the sol-gel and dip-coating technique. Coated and uncoated samples were then exposed to a sodium containing atmosphere at 1000°C for 360 hours to simulate typical industrial environment conditions. Structural post-exposure analyses based on weight loss measurements and mechanical tests indicated better corrosion resistance and strength retention for CMZP coated Si_3N_4 compared to as received and Mg-doped Al_2TiO_5 coated Si_3N_4 . This difference was attributed to the protective nature of the corrosion layer, which in the case of CMZP, significantly impeded the inward diffusion of oxygen to the Si_3N_4 surface.

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1.0 Introduction

Over the past fifty years substantial emphasis has been placed on the development of new and improved processes for generating, converting, and storing energy. Materials envisioned for these systems must not only possess excellent mechanical properties but also exhibit good chemical inertness in oxidizing environments. In this respect, silicon nitride (Si_3N_4) is a potentially good candidate for industrial heat exchangers in the High Temperature Advanced Furnace (HITAF) being developed under the DOE Combustion 2000 program. The desirable properties of Si_3N_4 are well known and include a high melting point, good thermal conductivity, high strength-to-weight ratio, high fracture strength and toughness and good chemical stability¹. Unfortunately, when subjected to coal combustion atmospheres containing alkali species, Si₃N₄ undergoes severe oxidation and eventually loses its properties ^{2,3}. Because oxides usually exhibit a better resistance to alkali corrosion than non-oxide materials^{4,5}, it was suggested that they could be applied as protective coatings producing cost effective composites, which combine both strength and corrosion resistance. Two oxides, magnesium doped aluminum titanate (Mg-doped Al₂TiO₅) and calcium magnesium zirconium phosphate (CMZP) with formula $(Ca_{0.6}, Mg_{0.4})Zr_4(PO_4)_6$ were selected as coatings because of their compatibility with Si₃N₄. Mg-Al₂TiO₅ is a well known oxide, which possesses a high melting point, low thermal conductivity, near zero coefficient of thermal expansion, and remarkable thermal shock resistance. Although very little information regarding its corrosion behavior is available in the literature, it was reported that the compound could impart good corrosion resistance. CMZP is a structural ceramic developed at Virginia Tech a few years ago and like Mg-doped Al₂TiO₅, it yields outstanding thermal properties and possibly good resistance to alkali corrosion. Previous work conducted at Virginia Tech have demonstrated the possibility to deposit Mg-Al₂TiO₅ and CMZP coatings on SiC and Si₃N₄ using the sol-gel and dip-coating techniques and exposures to alkali containing atmospheres have indicated improved alkali corrosion resistance 6,7,8 .

Within the framework of this study, the first key issue will involve the attainment and characterization of Mg-doped Al_2TiO_5 and CMZP oxide coatings deposited via sol-gel and dip-coating techniques. Then, the performance of coated and uncoated Si_3N_4 will be evaluated in terms of durability and strength retention using aging, weight loss measurements and flexural strength tests. Finally, in an effort to expand the existing knowledge on the coal combustion corrosion protection of Si_3N_4 , the degradation mechanism of coated samples will be investigated using physical and chemical analysis techniques.

2.0 Literature Review

2.1 Corrosion behavior of silicon nitride

At this point in time, it is well known to researchers that Si_3N_4 ceramics are unstable in the presence of oxygen at elevated temperature and that they rely on a thin film of SiO₂ for oxidation protection. For a given temperature the formation of this silica layer is conditioned by the partial pressure of oxygen as reported by Kim and other investigators ⁹⁻¹⁴. They indicated that at low oxygen partial pressure, active oxidation occurred resulting in the evolution of SiO gas, while at higher oxygen partial pressure, passive oxidation led to the formation of a protective SiO₂ layer. Normally, the silica layer can protect Si_3N_4 up to $1200^{\circ}C$, however, when subjected to high temperature alkali containing environments, it undergoes fast dissolution, exposing the surface of Si_3N_4 to severe attacks. The degradation mechanism whereby Si_3N_4 loses its structural properties has been widely investigated and is now relatively well understood. It consists of a continuous dissolution-oxidation process in which the alkali species readily dissolve the oxide scale forming an alkali silicate melt, while the oxygen diffuses through the liquid silicate melt to oxidize further the ceramic ¹⁵.

Several methods have been implemented to study the alkali corrosion of Si_3N_4 . Fox and Jacobson used the thin film test to model the situation encountered in heat engines ^{16,17}. The samples were airbrushed with a saturated solution of Na₂CO₃ or Na₂SO₄ and then, exposed to a pure flow of oxygen at 1000°C. In both cases, the investigators reported a three step corrosion mechanism, which first, consisted of the decomposition of Na₂CO₃ or Na₂SO₄ to form a sodium silicate melt by reaction with SiO₂, followed by a rapid oxidation of Si_3N_4 until the solubility limit of SiO_2 in the melt is reached, and finally a slowing of the reaction as a protective silica layer develops below the silicate layer.

Using the crucible test, Sato et al. studied the oxidation of different Si_3N_4 grades in K_2SO_4 and KCO_3 melts from 1150 to 1300 and 925 to 1150°C, respectively ^{3,18}. They examined the relationship between the degree of the corrosion and the reaction time and successfully correlated them via the surface chemical reaction-controlled shrinkage core model. Their results also indicated a much faster oxidation rate in nitrogen than in air and a strength reduction up to two third of the initial value.

To simulate aircraft turbine environments, Fox and Smialek devised the burner rig tests ¹⁹. The method consisted of subjecting the samples to a combustion flame seeded with 2 ppm Na impurities, which led to the deposition of a Na_2SO_4 melt. The investigators found that the chemical mechanism of attack was similar to the one observed with the thin film test. They found that Si_3N_4 was preferentially attacked at grain boundaries resulting in a 33 % strength reduction.

Similar results were also reported by G. R. Pickrell et al., who investigated the corrosion of silicon based ceramics in an NaNO₃ atmosphere ²⁰. Their results indicated that the oxidation rate of Si_3N_4 was 10^2 to 10^4 faster in a sodium containing atmosphere than in pure oxygen. Based on atomic absorption analyses, the authors also concluded that the alkali corrosion process was controlled by the interfacial oxidation of Si_3N_4 to SiO_2 .

2.2 The sol-gel technology

Treated as a scientific curiosity in 1845 when Ebelmen reported the synthesis of hydrous silica from silicon ester for the first time ²¹, the field of sol-gel is receiving much attention nowadays. Over the last thirty five years, this area of science has been

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extensively studied and its practice is now relatively well known 22 . The principal advantages of sol-gel processing include the ability to achieve oxygen and ionic stoichiometry during the formation reaction, to synthesize complex composition single phase materials, to form higher purity products through the use of high purity reagents, and to provide coatings over complex geometries including the insides of tubes. However, these advantages are to put in balance with the raw materials high cost, the long processing time involved, the non-uniformity of the films, and the formation of cracks upon drying 23 .

As its name indicates, the principle of the sol-gel technique consists of converting the sol which is a suspension of colloidal or polymeric particles in a solvent, into a semisolid phase known as gel. Commonly, the most preferred starting reagents are metal alkoxides, with general formula :

$$M(OR)_n$$

where $M = metal$
 $R = alkyl group such as methyl (CH_3), ethyl (C_2H_5), propyl (C_3H_7)$
or butyl (C₄H₉)
 $n = the valence of the metal atom.$

The transition from sol to gel involves two key steps, hydrolysis and condensation. Hydrolysis occurs by introducing water in the sol. In this process, the alkoxide groups (OR) are replaced stepwise by hydroxyl groups (OH) as summarized in figure 1. The hydrolysis rate was found to depend upon many factors. Indeed, the reaction can favorably be promoted by an increase in the charge density on the metal, the number of metal ions bridged by an hydroxo- or oxo-ligand, and the size of the alkyl groups ^{22,23}. Conversely, inhibition occurs as the number of hydroxo-ligand coordinating M increases or when the pH, temperature, or water and solvent concentration tend to favor the reverse reaction (esterification).

$$M(OR)_n + H_2O \qquad M(OH)(OR)_{n-1} + ROH$$

or $M(OR)_n + x H_2O \qquad M(OH)_x(OR)_{n-x} + x ROH \quad with \ 1 \quad x \quad n$

Figure 1 : Hydrolysis reaction.

The hydrolysation of the metal alkoxide particles is usually catalyzed by addition of an acid or base ²⁴. In acidic solution, the hydrolysis reaction proceeds by electrophilic attack ^{25,26}. As illustrated in figure 2 for tetraorthosilicate precursors, this mechanism features the attraction of a protonated water molecule (H_3O^+) to the negatively charged oxygen in the more basic alkoxide groups resulting in the substitution of an alkoxide group (OR) by an hydroxide group (OH). Conversely, in basic solutions the hydrolysis mechanism occurs by nucleophilic substitution ^{22,25}. In this case, the positively charged metal (M^+) is preferentially attacked by a negatively charged hydroxide (OH⁻) leading to the deprotonation of an hydroxo ligand as shown in figure 3.



Figure 2 : Acid catalyzed hydrolysis by electrophilic reaction mechanism.



Figure 3 : Base-catalyzed hydrolysis by nucleophilic reaction mechanism.

Once partially or totally hydrolyzed, the metal hydroxides undergo a stepwise polycondensation summarized as follows :

$2M(OR)_nOH$ $H_2O + (OR) M-O-M (OR)_n$

The condensation reaction involves hydroxyl groups and results in M-O-M linkages which, in turn, yield a three dimensional network (called gel) upon a polymeric weight and crosslinking-degree increase. The gel state is then best described as a viscoelastic material composed of interpenetrating solid and liquid phases ²⁴. Its structure is strongly dependent on the water content in the system and whether acid or base was used as hydrolysis catalyser. In acidic solution or for low water concentration, weakly crosslinked linear chains are produced, resulting in a soft gel which can be readily redispersed in solution. On the other hand, in based-catalyzed solutions, branched clusters are preferentially formed and their propency to coalesce is responsible for the gelation of the solution ²⁵.

However, the gel itself is not an end product. To obtain coatings, ceramic powders or monolithic shapes, the amorphous gel must be dried and crystallized at high temperatures. Most difficulties arise during the drying stage and are mainly caused by the removal of large amounts of solvent trapped in the polymeric network ²⁷. Indeed, the gel is prone to shrink by a large amount and capillary forces induce the formation of cracks.

To minimize these effects, gels are normally dried by slow evaporation and for coatings, the thickness usually must not exceed $10 \ \mu m$.

2.3 Sol-gel application

Since the early 1980's a better understanding and mastery of the sol-gel process has opened broad avenues for technological applications. There exist a multitude of areas, as diverse as biological supports or large mirrors for laser weapons in space, where the sol-gel technique is employed. The many area of interest are best summarized in the sol-gel tree of Dislich ²⁸ (see figure 4).



Figure 4 : Sol-gel tree.

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In this section emphasis will be placed on three promising commercial niches where the sol-gel process has been proved to be a competitive technique. These three areas deal with the production of ceramic powders, glass and coatings.

In the ceramic industry, advances in wet chemical techniques have created considerable enthusiasm mainly because of their potential to the produce ceramic powders. The driving force behind the use of sol-gel stems from the ability to prepare powders with a high purity, very fine spherical shape, and narrow distribution of particle size 28,29 . A high degree of purity is achievable since extremely pure starting materials are commercially available. However, their high energy cost production may be a limiting factor if saving energy (one of the chief advantage of the sol-gel process) is considered. The fine spherical shapes (e.g. 1 μ m), which yield a higher chemical activity and the correct particle size hardly attainable by milling are of prime importance for the densification of ceramics and are routinely obtainable through the use colloidal or base-catalyzed sols. It is well known to the ceramist that these important characteristics are key features for sintering to higher density and at temperatures much lower than those required in conventional processing. This is due to the fact that the rate of densification is inversely proportional to the radius of the particles and that for a given rate, the sintering temperature decreases with the particle size 23,30 .

Another area where the sol-gel technique has sparked widespread interest is the glass industry as evidenced by the large number of publications on TEOS (tetraorthosilicate) or TEOS related products. The glass industry can benefit from the sol-gel technology for two main reasons. First, it is possible to manufacture high-priced existing products, such as titanium silicate ULE glasses or graded-index optical fibers, more cheaply and with higher quality. It is noted that only expensive glass products are targeted since the high cost of raw materials (silicon or metal alkoxides are employed rather than silicon or metal oxides) make large quantity production commercially non viable. Therefore, the sol-gel process is by no means a substitute for heavy industrial

procedures, i. e. the production of flat glass, fiber glass, etc... However, when high-priced articles are concerned, sol-gel can be an alternative over conventional methods owing to some of its unique properties, which include high purity raw materials and low sintering temperatures. In this last case, considerable energy savings can be achieved because the porous structure of the gel does not require the attainment of liquidus temperatures to form the glass ³¹. The second reason which makes the sol-gel science appealing to the glass industry lies in its potential for innnovativeness. Indeed, a wide range of new products with desirable properties can not be obtained through the traditional melt route. For example, in contrast with classic processes, controlled hydrolysis-polymerization reactions can allow significant structural variation in the glass network without compositional alteration ²⁸. Wide perspectives for the synthesis of glasses with novel composition are opened since melt-related problems such as liquid immiscibility, phase separation, or crystallization upon cooling, are now suppressed.

Finally, the third area of application, which is also the oldest commercial exploitation of the sol-gel technique, deals with the preparation of coatings. Industrial applications include the development of thin films with specific mechanical, optical or electrical properties, as well as chemical or physical protective properties. There exist at least three coating methods, which are : dip-coating, spin-coating and spray-coating ²³. In the following paragraph, only the first technique is presented for it the most relevant to the current study. The advantages of using the sol-gel and dip-coating techniques for depositing thin films are well known and include the ability to coat complex shapes and large surfaces compared to vacuum coating techniques ^{31,32} and the acquisition of a relatively low cost non sophisticated equipment ^{23,33}. The disadvantages of the method lie in the high cost of the starting reagents, the long processing time involved, and the shrinkage and non-uniformity of the coatings. The dip-coating technique in itself is rather simple and consists in dipping, withdrawing, and firing the sample. The preparation of the sol usually requires a partial hydrolysis and the use of acid catalysts to synthesize a low viscosity medium with linear polymeric chains ^{30,34}. To form good uniform coatings,

C. J. Brinker et al. indicated that the withdrawing from the solution should be kept smooth and vibration-free. They found that the thickness of the films was mainly proportional to the lift rate and the viscosity of the sol. However, other factors such as the gravity and the surface tension must also be considered ³⁵. For multicomponent systems, it was reported that the rate of hydrolysis varied from a component to another. Therefore, to obtain films with uniform chemical composition, great care is required to allow bonds between the different alkoxides to form. Unfortunately, the hydrolysis of multicomponent systems is complex and very little is known for this subject ³³.

2.4 Mg-doped Al₂TiO₅ and CMZP ceramic oxides

2.4.1 Mg-doped Al₂TiO₅

Aluminum titanate, Al₂TiO₅, is a synthetic oxide ceramic well known for its high melting point, low thermal conductivity, near zero thermal expansion coefficient ($_{a} = +$ 9.8 10⁻⁶/°C, $_{b} = +$ 20.6 10⁻⁶/°C, $_{c} = -1.4 \times 10^{-6}$ /°C, $_{1} = 2 \times 10^{-6}$ /°C), and excellent thermal shock resistance ^{36,37}. With regards to its properties, Al₂TiO₅ is a good candidate for high temperature applications as reported by S. J. Charlton and M. J. Watts who tested the reliability of the ceramic for thermal insulating components in diesel engines swirl chambers ³⁸. They indicated that the components successfully completed the test without failure.

However, the use of aluminum titanate oxide has two major disadvantages. The first problem is related to the presence of microcracks due to internal stresses between grains. It was reported that if these microcracks account for the low thermal expansion coefficient of the oxide by absorbing the expansion of adjacent grain upon heating, they also moderate the room temperature strength of the material. To address this issue, some

researchers have developed compatible composites based on mullite-Al₂TiO₅ or Al₂TiO₅-ZrTiO₄-ZrO₂ systems in order to strengthen the ceramic ^{39,40} or synthesized submicromic powders by sol-gel to sinter pore-free compact oxides ⁴¹.

The second problem involves thermodynamics and comes from the decomposition of the compound into Al_2O_3 and TiO_2 between 800 and 1250°C. In the past, efforts have been focused on stabilizing the Al_2TiO_5 phase, and good results, i. e. almost pure $-Al_2TiO_5$ phases, were yielded by addition of small oxides amount such as MgO or Fe₂O₃ 42,43

Unfortunately, there is still no pertinent phase diagram for the alkali aluminum titanate system and very little information regarding its corrosion resistance is available. T. Sun et al. reported that coatings based on this compound could impart good corrosion resistance since no significant morphological changes upon exposure to sodium vapors were observed ⁶. These results were confirmed by M. Kang and Y. Shaokai who successfully developed magnesium-stabilized aluminum titanate coatings on silicon carbides to increase its oxidation resistance ^{7,8}.

2.4.2 CMZP

Similar to aluminum titanate, calcium magnesium zirconium phosphate (CMZP) is a good structural material possessing a high temperature-low thermal expansion coefficient, excellent thermal shock resistance, low thermal conductivity and possibly good corrosion resistance. CMZP belongs to the ultra low expansion NaZr₂(PO₄)₃ (NZP) family first reported in the literature by L. O. Hagman and P. K. Kierkegaard in 1968⁴⁴. NZP family-based materials owe their properties to an outstanding crystal structure composed of strongly bonded corner sharing ZrO₆ octahedra and PO₄ tetraedra in an open three dimensional framework, which allows a variety of ionic substitutions⁴⁵⁻⁴⁷. This particular feature has been exploited by many researchers to develop innovative materials such as $Na_3Zr_2Si_2PO_{12}$ (NASICON) for fast ionic conductors or new solid electrolytes where phosphor in the NZP was replaced by silicon sodium pairs ^{48,51}.

More recently, a great amount of research conducted at Virginia Tech has been aimed towards the synthesis of new high temperature structural ceramics with desirable thermal shock resistance. By substituting group I and II cations into the sodium position and by controlling the composition of $(Ca_{1-x},Mg_x)Zr_4(PO_4)_6$, the research group of Dr. J. J. Brown has been able to create a near zero thermal expansion material, with formula $(Ca_{0.6},Mg_{0.4})Zr_4(PO_4)_6$ ^{52,53}. The ceramic contracts along the a axis and expands along the c axis, yielding a bulk coefficient of thermal expansion of 0.1 10⁻⁶/°C. The corrosion resistance of silicon-based ceramic coated with CMZP was investigated by T. K. Li, M. Kang, and Y. Shaokai, and the three authors clearly witnessed reduced corrosion ^{7,8,54,55}.

3.0 Experimental Procedure

3.1 Surface pre-treatment

In order to enhance the adhesion of the film, commercially available hot pressed Si_3N_4 samples were pretreated to remove possible contaminants and form a silicon dioxide layer or OH groups on the substrate surface.

For CMZP coating, Si_3N_4 was soaked in an ultrasonic cleaner containing acetone for 1 hour, dried at 110°C for 2 hours and then immersed for 10 minutes in a solution containing 20% HF. Next, samples were washed with deionized water, dried at 110°C for 2 hours and calcined in air at 1200°C for 6 hours. Finally, the specimens were soaked in a 10% HCl solution for 10 minutes, then rinsed with deionized water and dried at 110°C for an additional 2 hours.

For Mg-doped Al_2TiO_5 coating, Si_3N_4 samples were first soaked in an ultrasonic cleaner containing deionized water for 30 minutes and then immersed in a 1:1 HNO₃ solution for 6 hours. Then they were washed with deionized water and dried at 110°C for 2 hours. Next, samples were calcined at 1200°C for 6 hours and soaked in a 10% HCl solution for 10 minutes. Finally, the specimens were rinsed with deionized water and dried at 110°C for an additional 2 hours.

3.2 Preparation of sol-gel solutions

3.2.1 CMZP sol-gel

The precursors selected for the sol-gel are calcium chloride (CaCl₂), magnesium perchlorate hexahydrate (Mg(ClO₄).6H₂O), zirconium propoxide (Zr(C₃H₇O)₄) and triethyl phosphate ((C₂H₅O)₃P(O)). The stoichiometric weight amounts calculated for the precursors are Ca : Mg : Zr : P = 1 : 1.393 : 28.110 : 16.413. First, CaCl₂ and Mg(ClO₄).6H₂O were mixed in ethyl alcohol and HCl was added drop by drop until a pH between 2.2 and 4.0 was reached. Then, $Zr(C_3H_7O)_4$ and $(C_2H_5O)_3P(O)$ were added dropwise. Water was added last and the pH readjusted. The CMZP concentration was 2.0 mol/L and the solution was clear with a slight yellow color.

3.2.2 Mg doped-Al₂TiO₅ sol-gel

The alkoxides selected for the sol-gel solution are magnesium nitrate hexahydrate $(Mg(NO_3)_2.6H_2O)$, aluminum tri-sec butoxide $(Al[C_2H_5CH(CH_3)O]_3)$ and titanium butoxide $(Ti[CH_3(CH_2)_3O]_4)$. The stoichiometric weight amounts calculated for the precursors are Al : Ti : Mg = 1 : 0.852 : 0.056. First, the three precursors were mixed and then a solution of ethyl alcohol and nitric acid with resultant pH between 1.0 and 4.0 was added dropwise to the precursor mixture. Water was finally added and the pH readjusted to keep the viscosity of the Mg_{0.1}Al_{1.8}Ti_{1.1}O₅ sol between 4.0 and 6.5 cp. The solution obtained was clear with a slight yellow color.

3.3 Coating techniques

3.3.1 Mg-doped Al₂TiO₅ coating

To obtain Mg-doped Al₂TiO₅ coatings, Si₃N₄ samples were immersed in the solgel solution for 30 minutes and withdrawn at a 4-8 cm/min lift rate. Hydrolysis was achieved by suspending the samples in a container with 40-80% RH at RT (room temperature) for 72 hours. The gel was then condensed in air at RT for an additional 48 hours and at 65 °C for 24 hours. Removal of all solvents and crystallization were achieved by employing a step controlled heating procedure and by firing the coated specimens at 1300°C for 10 hours. To reduce crack formation the specimens were slowly heated to 200°C, 300°C and 400°C at a heating rate of 1°C/min and remained at each step for 1.5 hours. Then, to prevent the crystallization of Al₂O₃ and TiO₂, they were rapidly heated to 1300°C at a rate of 10°C/min. After crystallization the specimens were cooled to RT at a rate of 5°C/min. Figure 5 shows the heat treatment schedule for Mg-doped Al₂TiO₅ coatings.

3.3.2 CMZP coating

 Si_3N_4 surface-treated specimens were soaked in the CMZP sol for 10 minutes and withdrawn at a 4-8 cm/min lift rate. The coated specimens were then hydrolyzed at room temperature (RT) and 40-80% relative humidity (RH) for 72 hours. Condensation was achieved by drying the samples at RT for an additional 48 hours and at 50°C for 24 hours. To remove residual solvent and organic components and crystallize the amorphous gel, the specimens were fired in air at 1200°C for 24 hours. The formation of cracks was reduced by using a step heating schedule. The samples were successively brought to 200°C, 300°C, 400°C and 500°C at a heating rate of 0.5°C/min and remained at each step for 2 hours. Next, they were heated up at rate of 5°C/min to 1000°C where they stayed for 4 hours and then fired at 1200°C.

For multiple coating deposition the samples were first dried at RT and 40-80% RH for 72 hours, then at RT for an additional 48 hours and finally at 50°C for 24 hours. Then, they were brought to 400°C where they remained for 6 hours. The rate of increasing and decreasing temperature was 0.5°C/min and 5°C/min, respectively. Successive coatings were applied using the same procedure before calcination at 1200°C. Figure 6 shows the CMZP coating process and heat treatment schedule in more details.

 $Mg(NO_{3})_{2}.6H_{2}O + Al[C_{2}H_{5}CH(CH_{3})O]_{3} + Ti[CH_{3}(CH_{2})_{3}O]_{4}$

$\mathbf{\Psi}$

add solution of ethyl alcohol and nitric acid

Ψ

add deionized water and adjust pH and viscosity

$\mathbf{\Psi}$

dip-coating

¥

RT and 40-80% RH for 72 h and air-dried for 48 h

↓ 0.5° C/min

65° C for 24 h

↓ *1°C/min*

200, 300, 400°C for 1.5h

↓ 10° C/min

1300°C for 10 h

Figure 5 : Heat treatment schedule for Mg-doped Al₂TiO₅ coatings.

$$CaCl_{2} + Mg(ClO_{4}).6H_{2}O$$

$$\downarrow$$
add solution of ethyl alcohol and HCl acid
$$\downarrow$$

$$Zr(C_{3}H_{7}O)_{4} + (C_{2}H_{5}O)_{3}P(O)$$

$$\downarrow$$

$$dip-coating$$
add deionized water and adjust pH
$$\downarrow$$

$$RT and 40-80\% RH for 72 h and air-dried at RT for 48 h$$

$$\downarrow 0.5^{\circ}C/min$$

$$50^{\circ}C for 24 h$$

x 3 x 3 ↓ 0.5° C/min ↓ 0.5° C/min 400° C for 6 h ↓ 5° C/min Room Temperature ↓ 0.5° C/min 200, 300, 400, 500° C for 1.5h ↓ 5° C/min 1000° C for 4 h ↓ 5° C/min

1200°C for 24 h

Figure 6 : Heat treatment schedule for CMZP coatings.

3.4 Thermal shock resistance test

The thermal shock resistance of coated and uncoated specimens with dimension of $5 \times 5 \times 3$ mm was investigated. Five groups of three samples were heated to 600, 700, 800, 900, and 1000°C, respectively, and then quenched in water at 25°C. The surface microstructure of the coatings and their adhesion to the substrate was examined by scanning electron microscopy (SEM), (International Scientific Instrument, model SX-40).

3.5 Alkali corrosion tests

The most appropriate corrosion test for simulating coal combustion conditions in real industrial systems is the laboratory film test. Two variations of this test were devised in this study.

For four-point bending strength measurements, 3 x 4 x 50 mm Si₃N₄ MOR (modulus of rupture) bars coated with CMZP and Mg-doped Al₂TiO₅, respectively, were first heated to 200°C and dip-coated in a NaNO₃ saturated aqueous solution to deposit a sodium containing film. The amount of salt adhering to the surface was calculated to be 3-4 mg/cm². Then, the samples were exposed to an atmosphere containing a constant 8 vol.% NaNO₃ concentration at 1000°C for 48 h. A scheme of the apparatus used for the alkali corrosion experiment is given in figure 7. Although Na₂SO₄ is the most common melt encountered in industrial systems, NaNO₃ (Aldrich, ACS Reagent) was preferred for the alkali source because of its high vapor pressure in the 700-800°C temperature range as compared to NaCO₃ or Na₂SO₄²⁰. As illustrated in figure 7, the apparatus consists of two separate heating zones. On the gas inlet side an alumina boat filled with NaNO₃ was heated to 720°C ± 10 using high temperature heating tapes coupled with a potentiometer and a K type thermocouple gauge. A flow rate of compressed air, fixed at 86 cm³/min, was used to carry the alkali containing species in the second heating zone, the reaction

zone, where the temperature was maintained at 1000° C. Prior entering the alumina tube, the compressed air was filtered to remove moisture and CO₂. This was achieved by using a four compartment plastic tube filled with silica gel, drierite, activated alumina and silica gel, respectively.

To investigate the strength degradation as a function of time, a 1000° C and 360° hour corrosion experiment was conducted. 3 x 4 x 24 mm Si₃N₄ MOR bars were heated to 200°C, dip-coated in a NaNO₃ saturated aqueous solution and then, placed in a furnace containing a crucible filled with sodium nitrate. By measuring the weight loss of NaNO₃ and assuming that the vapor behaves like an ideal gas the concentration was calculated to be 4-5 vol%. A schematic of the furnace is given in figure 8.



Figure 7 : Schematic of the alkali corrosion apparatus used with four point bending test.



Figure 8 : Schematic of the alkali corrosion apparatus used for the aging test.

3.6 Corrosion resistance evaluation

3.6.1 Three- and four-point flexural tests

The effect of the alkali corrosion on the mechanical properties of as received and coated Si_3N_4 specimens was examined by three- and four-point bending using an ATS model 1120 universal testing machine. Room temperature four-point flexural strength tests were performed on 3 x 4 x 50 mm MOR bars at a crosshead of 0.5 mm/min with inner and outer spans of 20 and 40 mm, respectively. For samples with dimensions 3 x 4 x 25 mm, the flexural strength was determined using the three-point bending test. The bend test had an outer span of 20 mm, an inner span of 10 mm, and a loading rate of 0.2 mm/min.

3.6.2 Weight loss measurements

To study the weight loss after corrosion, the specimens were first washed in distilled water at 100°C to remove water soluble phases such as residual salts and sodium silicates, and then etched in 10% HF to remove the corrosion product layer. Prior to weighing, the samples were dried in an oven for 2 hours. This entire procedure was repeated until no change in weight was observed.

4.0 Results and Discussion

4.1 Surface pre-treatment

Contact angle tests were conducted to assess the effectiveness of the surface preparation. Five measurements were performed on each samples using a 2 ml deionized water drop and the results for Si_3N_4 as received, Si_3N_4 surface treated for CMZP and Mg-doped Al_2TiO_5 , are given in Table 1. The large difference in contact angle before and after the surface treatment suggests that the adhesion of the coatings on the surface was significantly enhanced. Good wetting of the surface and spreading of the water drop were observed for both surface preparation as indicated by the small contact angle (< 5°).

	Si_3N_4 as received	Si ₃ N ₄ surface treated	Si_3N_4 surface treated
		for CMZP	for Mg-doped
			Al ₂ TiO ₅
Contact angle (°)	70.7	< 5	< 5

Table 1 : Contact angle for as-received Si₃N₄ and Si₃N₄ surface treated for CMZP and Mg-doped Al₂TiO₅.

After calcination at 1200°C for 6 hours, the formation of a 1 μ m thick silica layer was observed. Figure 9 shows a cross section and corresponding EDX (model ISI SX-40, beryllium window) elemental mappings for Si₃N₄ surface treated. The presence of Al and

Y, probably coming from the sintering aid, was also detected near the surface, suggesting that the silica layer is not pure.



Figure 9 : SEM photomicrograph of a fractured surface for a surface-treated Si_3N_4 and corresponding elemental mappings.

4.2 Sol-gel coatings characterization

4.2.1 Sol-gel derived powders

In the early stage of this research, it was necessary to confirm whether the sol-gel procedure devised successful synthesized the desired compounds. For this purpose, x-ray diffraction was used (International Scientific Instrument, model SX-40) and the patterns of the calcined powders derived from the CMZP and Mg-doped Al₂TiO₅ sol-gels are presented in figure 10. Using x-ray data given for $(ZrO)_2P_2O_7$ (ZP), $CaZr_4(PO_4)_6$ (CZP), MgZr₄(PO₄)₆ (MZP), (Ca_{0.6},Mg_{0.4})Zr₄(PO4)₆ (CMZP), TiO₂, Al₂O₃ and Mg-doped Al₂TiO₅ powders ^{42,43,56,57}, it was possible to identify the phases present in the synthesized sol-gels.

For CMZP powder calcined at 1200°C for 24 hours, the x-ray diffraction pattern indicated a nearly pure CMZP phase with the presence of minor peaks of CZP, ZP, and MZP. Their presence may be attributed to an excess of calcium, magnesium and zirconium precursors.

For Mg-doped Al_2TiO_5 , XRD peaks yielded are similar to those reported by previous workers ^{6,7,8}. No peaks of TiO₂ and Al_2O_3 were evidenced, suggesting that the addition of Mg²⁺ succeeded in stabilizing the compound.

In both cases, the presence of sharp peaks indicates that the compounds were well crystallized.



Figure 10 : XRD patterns of a) CMZP calcined powder, b) Mg-doped Al₂TiO₅ calcined powder.

4.2.2 CMZP coating

Homogeneous and crack-free CMZP coatings were successfully deposited using the sol-gel and dip-coating techniques. Figure 11 presents a photomicrograph of the coating microstructure at magnification 2000 obtained by SEM (model ISI SX-40, electron accelerating voltage 20 kV). The film is composed of 1-3 µm spheroid grains, which are uniformly distributed on the surface. The EDX elemental maps show a uniform distribution of Ca, Mg, Zr, and P in each grain suggesting that the CMZP phase was achieved. SEM inspection revealed that the formation of crack-free films was strongly dependent on the solution concentration and the lift rate. To avoid poor coverage of the surface or spalling of the coating, the solution concentration and the withdrawing rate were to be kept between 1.5 to 3.0 mol/L and 4.0 to 6.5 cm/min, respectively. Good surface coverage of Si₃N₄ was obtained after the application of three coatings, using a solution with concentration 2.0 mol/L and a lift rate of 6.5 cm/min. The film thickness was also influenced by the solution concentration and was found to vary between 1 and 5 µm as illustrated on the cross-section shown in figure 12. As expected the formation of the CMZP films was evidenced by the distribution of CA, Mg, Zr, P and O elements at the surface, however, the possibility of a substantial reaction between CMZP, SiO₂, and the sintering additives, Al₂O₃ and Y₂O₃, is not excluded since EDX analyses also revealed the presence of Si, Al, and Y. Besides, the detection of Ca and Mg in the bulk of Si_3N_4 suggests that a diffusion process, most likely along the grain boundary, may have taken place for these two elements.



Figure 11 : SEM photomicrograph of CMZP coating.



Figure 12 : SEM photomicrograph of a fractured surface for Si_3N_4 coated with CMZP and corresponding elemental mappings.

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4.2.3 Mg-doped Al₂TiO₅ coating

For Mg-Al₂TiO₅ coatings, key parameters to avoid cracks and aggregation were the solution viscosity, which was kept between 4.0-6.5 cp, and the lift rate set at a speed of 6.5 cm/min. Unfortunately, Si_3N_4 samples coated with Mg-doped Al₂TiO₅ sol-gel did not give the expected coating as shown in figure 13. The SEM photomicrograph features an aluminum titanium silicate glassy phase with the presence of needle-like particles at the surface. EDX analyses indicate that these particles have higher level of yttrium than the surrounding matrix. Similar needle-like particles were also observed by other investigators using a silicon nitride grade containing yttria sintering agent ⁵⁸. Using x-ray diffraction, the compound was identified as yttrium dissilicate, Y_2SiO_5 , which is the result of the oxidation of yttria diffusing from the grain boundary to the surface. The driving force for the diffusion is the necessity to equilibrate the chemical composition of the glassy phase formed. EDX analyses also traced the formation of a phosphorous compound, which could not be identified. It is believed that the phosphor was coming from contaminants present in the furnaces.



Figure 13 : SEM photomicrograph of Mg-doped Al₂TiO₅ coating.

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4.3 Thermal shock resistance

The thermal shock resistance of coated and uncoated samples was examined for temperatures ranging from 500 to 1000°C. CMZP and Mg-doped Al₂TiO₅ coatings should yield an excellent thermal shock resistance since their respective coefficient of thermal expansion (0.1-2 10^{-6} /°C for CMZP and 2-3 10^{-6} /°C for Mg-doped Al₂TiO₅) matches the one of Si₃N₄ (3 10^{-6} /°C). The experimental results presented in Table 2 are consistent with the above analysis and the data provided by previous workers ^{7,8,54,55}. SEM inspection of the specimens' surface confirmed that cracks formed between 700 and 800°C. However, no spalling was observed indicating a good adhesion between Si₃N₄ and the coatings as shown in figure 14. It is believed that the coatings may even exhibit higher thermal shock resistance since cracks observed in the film seem to have been induced by the propagation of cracks generated in Si₃N₄ bulk as results with uncoated samples indicate.

Temperature (°C)	500	600	700	800	900	1000
Si ₃ N ₄	no cracks	no cracks	no cracks	cracks	cracks	cracks
CMZP	no cracks	no cracks	no cracks	cracks	cracks	cracks
Mg-doped Al ₂ TiO ₅	no cracks	no cracks	no cracks	cracks	cracks	cracks

Table 2 : Thermal shock resistance of coated and uncoated Si₃N₄ samples.

(b)



Figure 14 : Surface of microstructure of a) CMZP and b) Mg-doped Al_2TiO_5 after thermal shock test at 800°C.

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4.4 Effect of the corrosion reaction on the microstructure

One of the properties of silicon based ceramics is their ability to develop a protective silica layer when oxidized at high temperatures. In air, this protective layer usually impart a good oxidation resistance to Si_3N_4 . Unfortunately, it was observed that the SiO_2 protective thin film underwent fast dissolution when subjected to high temperature alkali containing atmospheres, exposing Si_3N_4 to further attack. The corrosion mechanism in the presence of sodium compounds has been widely studied and consists of a series of step reactions involving first the dissolution of the solid silica layer to form a liquid non protective sodium silicate scale as shown in reaction (1). Then the reaction proceeds by oxidation of the Si_3N_4 ceramic through inward diffusion of oxygen and outward diffusion of N_2 gas product according to reaction (2). The silica layer formed after oxidation dissolves readily in contact with the sodium silicate phase as can be seen from reaction (3) and from that point the corrosion reaction goes on with the repetition of step 2 and 3.

$$Na_2O + x SiO_2 \qquad Na_2O.x SiO_2 \tag{1}$$

$$Si_3N_4 + 3O_2 = 3 SiO_2 + 2 N_2$$
 (2)

$$SiO_2 + Na_2O.x SiO_2 \qquad Na_2O.(x+1) SiO_2 \qquad (3)$$

To alleviate or minimize the corrosion reaction, it is believed that the refractoriness of the sodium silicate layer should be increased. This may be achieved by introducing other compounds in the reaction layer via the application of a coating prior corrosion.

4.4.1 Corrosion of CMZP coated samples

Si₃N₄ samples coated three times with CMZP sol-gel were tested in an NaNO₃ atmosphere at 1000°C for 48 h using the apparatus shown in figure 7. The microstructural changes of the coated samples were studied with scanning electron microscopy, x-ray energy dispersive spectrometry, and x-ray diffraction. The examination of the specimens' surface after corrosion reveals some important microstructural effects. Figure 15 shows the EDX spectra of the surface of CMZP coated silicon nitride before and after corrosion. The appearance of a strong Na peak in the EDX spectrum of the corroded coupon indicates that some chemical reactions must have taken place during the 48 hour test. The surface morphology yielded after corrosion clearly suggests that the CMZP coating has been partially attacked by the NaNO₃ melt. As can be observed in figure 15, the corrosion product layer features nodular and needle-like particles along with some coarse and smooth areas. Based on EDX elemental analysis, it was possible to identify the different elements present on the surface and to determine their distribution as shown in figure 16 a). Using these information, an attempt was made to label the different peaks yielded by XRD. For the uncoated Si₃N₄ specimen the corrosion product layer primarily consists of sodium silicate phase, Na₂O.xSiO₂ while for specimen coated with CMZP, XRD pattern evidenced the presence of other silicate phases along with sodium silicate. Table 3 summarizes the different particles observed for CMZP coated Si_3N_4 and their possible identification.

particle or area element detected		possible phase identification
	with EDX	
needle like particle	Al, Si, O, Na	NaAlSiO ₄ (sodium aluminum silicate)
nodular particle	Y, Si	Y ₂ SiO ₅ (yttrium silicate)
coarse area	Si, Na, O	Na ₂ O.xSiO ₂ (sodium silicate)
smooth region	Ca, Zr, P, Si, O	SiZr (zirconium silicate)
		CaZr(PO ₄) ₂ (calcium zirconium
		phosphate)
		CaZrSi ₂ O ₇ (calcium zirconium silicate)
		Ca ₂ SiO ₇ (calcium silicate)

 Table 3 : Possible phases present in the corrosion product layer.





Figure 15 : EDX spectrum of CMZP coatings a) before corrosion. b) after corrosion.



needle-like particle (Al, Si, O, Na)









Figure 16 : a) SEM photomicrograph of CMZP coating after corrosion.b) corresponding EDX elemental mapping.

To study the attacked microstructure of the ceramic, the corrosion products were first removed during a two hour treatment in H₂O. After the water leach, the corrosion scale was identified as an aluminum yttrium silicate phase and an aluminum yttrium silicate phase with the presence of Mg, Ca, Zr, P, and O for Si₃N₄ as received and Si₃N₄ coated with CMZP, respectively. The morphology of the corrosion scale for uncoated and coated specimens are depicted in figure 17. As it can be seen, the two photomicrographs yield interesting differences. For the uncoated sample pores or pittings are observed in the silicate layer whereas a relatively unattacked corrosion scale is depicted for the coated specimen. This result suggests that over a 48 hour corrosion period, CMZP coatings have significantly reduced the extent of the corrosion.

Finally, the corrosion scale was removed using a mild HF treatment (15 min, 10%HF, 60 °C) ^{8,20}. Photomicrographs of the attacked morphology are presented in figure

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18. As expected two different features were evidenced. For the uncoated Si_3N_4 specimen, -silicon nitride grains were observed, suggesting an attack of the ceramic at the grain boundary as reported by many other investigators ¹⁶⁻²⁰ while no or very little attack at the grain boundary phase was evidenced with CMZP coating.



(a)







Figure 18 : SEM photomicrographs of the attack morphology obtained after mild HF (15 min, 10%HF, 60°C) treatment for a) uncoated Si_3N_4 , and b) Si_3N_4 coated with CMZP.

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4.4.2 Corrosion of Mg-doped Al₂TiO₅ coated samples

SEM photomicrograph and corresponding elemental mappings obtained for Mgdoped Al_2TiO_5 corroded specimens are presented in figure 20 and indicate that the needle like particles are preferentially attacked by the NaNO₃ melt. The attacked morphology obtained after water leach and a mild HF treatment (see figure 21), features some silicon nitride grains, which tend to suggest that the coating did not preserve Si₃N₄.





Figure 19 : SEM photomicrograph of the corrosion product layer and associated elemental maps for Si_3N_4 coated with Mg-doped Al_2TiO_5 and corroded at 1000°C for 48 h in a NaNO₃ containing atmosphere.



Figure 20 : SEM photomicrograph of the attacked microstructure obtained after water leach and mild HF treatment for Si_3N_4 coated with Mg-doped Al_2TiO_5 and corroded at 1000°C for 48 h in a NaNO₃ containing atmosphere.

4.4.3 Long time exposure

For longer exposure time, the dissolution of the coatings proceeds further and a thick silicate phase forms indicating the presence of a liquid melt at the oxidation temperature. After 96 hour exposure, the morphologies of the corroded samples examined by SEM were similar for coated and uncoated Si_3N_4 . The presence of holes produced by the evolution of N_2 gas escaping through the corrosion layer as bubbles was clearly evidenced at the surface of the glassy phase. Their number witnessed the extent of the oxidation attack and was significantly larger for silicon nitride as received and coated with Mg-doped Al_2TiO_5 .

For Si₃N₄ as received specimens, the associated x-ray maps shown in figure 21 yielded an even distribution of Si, O, Al, and Na, indicating the formation of a sodium aluminum silicate phase containing relatively small quantity of Y. For CMZP coatings, the corrosion scale was formed of a sodium aluminum silicate phase containing large amount of Zr and P. Ca, Mg, and Y were also incorporated in the film but in a lesser extent as indicated in figure 22. For Mg-doped Al₂TiO₅ coatings, it was determined from Si, O, Al and Na maps that the corrosion layer consisted primarily of a sodium aluminum silicate phase with small quantity of Mg, Ti, and Y as featured in figure 23. These results demonstrate that the chemical nature of the corrosion layer can be successfully modified via the application of a coating prior to exposure. It is believed that upon oxidation the coating dissolves in the melt making possible the incorporation of particular compounds in the oxidation scale.

Besides, in order to assess whether the corrosion proceeds via uniform surface recession or via enhanced attack in localized regions as the evolution of gases would tend to suggest, the microstructure of the ceramics was examined after removal of the corrosion product by a dilute HF treatment. SEM inspection indicated that only a few bubbles were correlated with some pits and it was observed that the pitting phenomena was of relatively limited importance compared the uniform surface recession mechanism. The mode of attack is therefore similar to the one encountered with as received Si₃N₄ and it consists in the consumption of the ceramic at the grain boundary phase. It is proposed

that accelerated chemical reactions are favored by the aggregation of Al_2O_3 and Y_2O_3 which act as a softening agents by lowering the solidus temperature of the grain boundary phase ²⁰.



Figure 21 : Fractography and corresponding EDX mappings of as received Si_3N_4 after 216 hour corrosion at 1000°C.



Figure 22 : Fractography and corresponding EDX mappings Si_3N_4 coated with CMZP after 216 hour corrosion at 1000°C.



Figure 23 : Fractography and corresponding EDX mappings of Si_3N_4 coated with Mg-doped Al_2TiO_5 after 216 hour corrosion at 1000°C.

4.5 Alkali corrosion resistance

The influence of the alkali corrosion on the fracture strength of silicon based ceramics is assessed in this section. Strength degradation of Si_3N_4 in harsh environments is of prime concern because it can set serious limitations to its use in structural applications. The four point bending strength of coated and uncoated specimens before and after 96 hour exposure to sodium vapors is presented in figure 24 and table 4. The application of the coatings did not significantly affect the strength of Si_3N_4 . However, after the corrosion test, the strength of all the samples was found to decrease below their initial values. The standard deviation error presented in table 4 and calculated with the Student's t test for a level of confidence of 95%, indicate that the strength reduction observed are significant. A comparison of the three sets of specimens with uncoated Si_3N_4 taken as reference (-14.4% of initial strength) show the least strength degradation for CMZP (-7.1% of initial strength) after corrosion test. On the other hand, the formation of the aluminum titanium silicate glassy phase obtained with Mg-doped Al_2TiO_5 coatings has, in a large extent, reduced the fracturel strength of Si_3N_4 (-14.9% of initial strength).



Figure 24 : Four point bending fracturel strength of coated and uncoated Si₃N₄ before and after 96 hour corrosion at 1000°C.

Strength (MPa)						
	Si ₃ N ₄	CMZP	Mg-doped Al ₂ TiO ₅			
Before Corrosion	710.7 ± 15.6	691.1 ± 12.7	686.9 ± 15.1			
After Corrosion	608.3 ± 13.2	642.1 ± 13.8	584.5 ± 18.8			

Table	4:	Alkali	corrosion	resistance	of	coatings.
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The three-point bend flexural strength and weight loss measurements as a function of time were also investigated and are shown in figure 25 and 26, respectively. The same trend as with the four point bending test was observed. With regard to both strength degradation and weight loss, CMZP exhibited the best oxidation resistance after aging, followed by as received and Mg-doped Al₂TiO₅ coated samples. Within experimental error, the measurements of the flexural strength reduction after the 360 hour corrosion are -31%, -26%, and -32% of the initial strength and the weight loss is -8.0%, -6.3%, and -7.7% for as received Si₃N₄, Si₃N₄ coated with CMZP and Si₃N₄ coated with Mg-doped Al₂TiO₅, respectively. These results indicate that the incorporation of Ca, Mg, Zr, and P in the corrosion scale resulted in a more refractive layer, which can significantly prevent the corrosion. Conversely, the addition of Al, Mg, and Ti in the corrosion products has the opposite effect, suggesting the promotion of the oxygen diffusivity throughout the reaction scale. However, it is extrapolated that for longer exposure time, further strength reduction will occur for the three sets of samples as the material surface recession proceeds and that specimens coated with CMZP will eventually yield the same flexural strength as uncoated specimens since the relative quantities of Mg, Ca, Zr, P, and O are bound to decrease with respect to the increasing amount of sodium silicate continuously incorporated in the corrosion scale.

Regardless of the coatings, weight loss measurements seem to indicate a two step kinetic process for the oxidation reaction. Indeed, as shown in figure 26, a rapid consumption of the ceramic is evidenced by a substantial increase in the weight loss for all samples over the 144 first hour of testing. This stage is most probably associated with the dissolution of the coatings or the silica layer and the formation of a liquid melt through which oxygen diffuses and readily oxidizes Si_3N_4 . Then, the weight loss curves seem to reach a plateau, indicating a slowing of the oxidation. This result may be attributed to the saturation of the corrosion scale by silica, which would allow the formation of a protective silica layer under the melt.

To understand the strength degradation from a mechanical standpoint, the fracture surface of broken specimens was examined. For all samples, SEM fractography analyses revealed the presence of bubbles in the fractured region. These lenticular occlusions created by the release of gases during the oxidation appeared to be at the origin of the crack propagation as featured in figure 21. This mechanism of failure is well known in mechanics and is explained in terms of stress concentration around the pore-like defects. Generally speaking, it is accepted that the strength of ceramics is strongly influenced by the pore size (10 μ m) and their content. Duckworth has proposed an experimental relationship between strength and porosity ⁵⁹, in which the strength decrease is directly correlated to the pore size and content as indicated in the following equation :

$$_{p} = _{o} e^{-BP}$$

with _p the strength of the ceramic with porosities

_o the strength of the ceramic without porosities

B a constant which depends on the distribution and morphology of the pore P the fractional pore content

Based on this equation, the higher fracturel strength yielded by Si_3N_4 coated with CMZP after corrosion can be attributed to a significantly smaller number of bubbles in the corrosion scale.



Figure 25 : Three point bend flexural strength as a function of time after sodium vapor corrosion at 1000°C.



Figure 26 : Weight loss measurements as a function after sodium vapor corrosion at 1000°C.

5.0 Conclusions

In this work, $(Ca_{0.6}, Mg_{0.4})Zr_4(PO_4)_6$ (CMZP) and Mg-doped Al₂TiO₅ coatings were deposited on silicon nitride using the sol-gel and dip-coating techniques.

For CMZP, homogeneous crack-free films and a good coverage of the surface were achieved after the application of three coatings using a solution concentration of 2.0 mol/L and a lift rate of 6.5 cm/min. EDX compositional characterization identified CMZP as the main phase and SEM microstructural examination evidenced the formation of 1 to 3 μ m thick films composed of 2-3 μ m spheroid grains.

For Mg-doped Al_2TiO_5 , key parameters to obtain crack-free coatings were the viscosity, which was kept between 4.0 and 6.5 cp and the lift rate fixed at 6.5 cm/min. However, the compound reacted with the silica layer which was intentionally developed on Si_3N_4 surface resulting in the formation of an aluminum titanium yttrium silicate glassy phase.

To simulate industrial coal combustion conditions, coated and uncoated specimens were then exposed to sodium nitrate (NaNO₃) containing atmospheres at 1000°C. For all specimens, the oxidation attack resulted in the dissolution of the coatings or the silica layer and an alkali corrosion silicate scale containing the elements incorporated in the coatings was observed. The mode of degradation was found to occur via a surface recession mechanism caused by the attack of silicon nitride at the grain boundary.

Finally, the mechanical properties before and after corrosion were evaluated in terms of durability and strength retention using aging, weight loss measurements and flexural strength tests. SEM investigation showed that the formation of trapped bubbles resulting from the evolution of gases during the oxidation reactions created pore-like defects. In most cases, these occlusions were identified as the major cause of failure. Strength degradation and weight loss comparison indicated that samples coated with CMZP retained better their structural properties than uncoated or Mg-doped Al_2TiO_5 coated Si_3N_4 . This difference was attributed to the ability of CMZP to form upon corrosion, a more refractive silicate layer, which significantly reduces the inward diffusion of oxygen and thus, the extent of the corrosion.

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Vita

Thierry Huu Chi Nguyen was born on September 7, 1972 in Saigon, Vietnam. At the age of six, he moved to Lyon, France, where he remained for the rest of his adolescence and teenage life. He attended the University of Claude Bernard of Lyon from 1991 to 1993 where he gained with honor a general diploma in physics, ranking 10th out of 300 students. Then, he entered a French engineering school, the Institut des Sciences et Techniques de l'Ingénieur de Lyon (ISTIL), where after three years he gained his bachelor degree (1996). As partial fulfillment of his last year at ISTIL, he decided to make a six month practical training at the Center for Adhesive and Sealant Science located at Virginia Polytechnic Institute and State University, where he worked under the supervision of Dr. J. G. Dillard on the durability of titanium alloy composites. Following this first American experience, he ceased the opportunity, which is granted to every French, to make his military service abroad and completed at the same time a master's degree in Materials Science and Engineering. Under the guidance of Dr. J. J. Brown, he conducted his research on the protection of ceramic materials and extended his knowledge in the field of coatings.