CORROSION RESISTANT COATINGS FOR SiC AND Si₃N₄ CERAMICS

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ABSTRACT

It is the goal of this program to 1) develop coatings for SiC and Si₃N₄ that will enhance their performance as heat exchangers under coal combustion conditions and 2) to conduct an in-depth evaluation of the cause and severity of ceramic heat exchanger deterioration and failure under coal combustion conditions.

Part 1

Thin film coatings of (Ca_{0.6}Mg_{0.4})Zr₄(PO₄)₆ (CMZP) and Mg-stabilized aluminum titanate (Mg-Al₂TiO₅) on dense SiC substrates were investigated using sol-gel coating techniques. The thickness and quality of both CMZP and Mg-Al₂TiO₅ coatings were found to depend on the solution concentration and lift rate. Double coatings were applied to obtain homogeneous and crack-free coatings. The quality of double coatings was influenced by different first and second coating thickness. The CMZP coated samples were fired in controlled atmospheres to have the pure CMZP phase. Unhydrolyzed solution of Mg-Al₂TiO₅ was utilized instead of hydrolyzed solution to improve the quality of Mg-Al₂TiO₅ coatings. An aging process was found to improve the quality of CMZP and Mg-Al₂TiO₅ coatings. SiC samples coated with CMZP and Mg-Al₂TiO₅ exhibited good thermal shock resistance and greatly improved the high temperature alkali corrosion resistance.

Part 2

Silicon nitride (Si₃N₄) 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 CMZP and Mg-doped Al₂TiO₅ were successfully deposited on Si₃N₄ 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 Si₃N₄ compared to as-received and Mg-doped Al₂TiO₅ coated Si₃N₄. 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 Si₃N₄ surface.

Table of Contents

Abstract	i
Part 1 Development of Coatings for SiC and Si₃N₄	1
Introduction	1
Literature Review	1
<i>Silicon Carbide</i>	1
<i>(Ca_{0.6}Mg_{0.4})Zr₄(PO₄)₆ (CMZP)</i>	2
<i>Aluminum Titanate</i>	3
<i>Sol-Gel Techniques</i>	3
Experimental Procedures	4
<i>Substrate Pre-Treatment</i>	4
<i>Preparation of CMZP Solution</i>	4
<i>Preparation of Mg-Al₂TiO₅ Solution</i>	4
<i>Coating Techniques</i>	5
<i>CMZP Coating</i>	5
<i>Mg-Al₂TiO₅ Coatings</i>	5
<i>Thermal Shock Resistance Test</i>	5
<i>Alkali Corrosion Resistance Test</i>	8
<i>100-Hour Slagging Combustion Test</i>	8
<i>Coating Procedure</i>	8
<i>Test Conditions</i>	9
<i>Measurements of Samples</i>	10
<i>Aging Process</i>	10
Results and Discussion	13
<i>Characterization of Coatings on SiC</i>	13
<i>CMZP Coatings</i>	13
<i>Mg-Al₂TiO₅ Coatings</i>	22
<i>Obtaining Pure CMZP Phase</i>	31
<i>Improving Mg-Al₂TiO₅ Coating Procedure</i>	38
<i>Thermal Shock Resistance</i>	39
<i>CMZP Coatings</i>	39
<i>Mg-Al₂TiO₅ Coatings</i>	42
<i>Alkali Corrosion Resistance</i>	44
<i>CMZP Coatings</i>	44
<i>Mg-Al₂TiO₅ Coatings</i>	48
<i>100-Hour Slagging Combustion Test</i>	51
<i>CMZP Coated Samples</i>	51
<i>Mg-Al₂TiO₅ Coated Samples</i>	51
<i>Aging Process</i>	58
<i>Thermal Shock Resistance Test</i>	58
<i>Alkali Corrosion Resistance Test</i>	63
Conclusions	69
Part 2 Evaluation of Cause and Severity of Ceramic Heat Exchanger Deterioration and Failure Under Coal Combustion Conditions	71

Introduction	71
Literature Review	71
<i>Corrosion Behavior of Silicon Nitride</i>	71
<i>Sol-Gel Technology</i>	72
<i>Sol-Gel Application</i>	74
<i>Mg-doped Al₂TiO₅ and CMZP Ceramic Oxides</i>	76
<i>Mg-doped Al₂TiO₅</i>	76
<i>CMZP</i>	77
Experimental Procedure	77
<i>Surface Pre-treatment</i>	77
<i>Preparation of sol-gel solutions</i>	78
<i>CMZP sol-gel</i>	78
<i>Mg-doped Al₂TiO₅ sol-gel</i>	78
<i>Coating Techniques</i>	78
<i>Mg-doped Al₂TiO₅ coating</i>	78
<i>CMZP coating</i>	79
<i>Thermal Shock Resistance Test</i>	79
<i>Alkali Corrosion Tests</i>	79
<i>Corrosion Resistance Evaluation</i>	83
<i>Three- and Four-point Flexural Tests</i>	83
<i>Weight Loss Measurements</i>	83
Results and Discussion	83
<i>Surface Pre-Treatment</i>	83
<i>Sol-gel Coatings Characterization</i>	85
<i>Sol-gel derived powders</i>	85
<i>CMZP coating</i>	85
<i>Mg-doped Al₂TiO₅ coating</i>	89
<i>Thermal Shock Resistance</i>	89
<i>Effect of the corrosion reaction on the microstructure</i>	90
<i>Corrosion of CMZP coated samples</i>	92
<i>Corrosion of Mg-doped Al₂TiO₅ coated samples</i>	96
<i>Long time exposure</i>	96
<i>Alkali Corrosion Resistance</i>	101
Conclusions	107
References	109

List of Figures

Figure 1. Heat treatment schedule for CMZP coating dense SiC	6
Figure 2. Heat treatment schedule for Mg-Al ₂ TiO ₅ coating dense SiC	7
Figure 3. Isometric drawing of combustion test system	11
Figure 4. SEM micrographs of as-received SiC samples	14
Figure 5. SEM micrographs of CMZP coatings under high solution Concentration of 0.2 mol/L and lift rate of 6.5 cm/min	15
Figure 6. SEM micrographs of CMZP coatings under the low solution Concentration of 0.05 mol/L and lift rate of 6.5 cm/min	17
Figure 7. SEM micrographs of CMZP coatings under medium solution Concentration of 0.1 mol/L and lift rate of 6.5 cm/min	19
Figure 8. SEM micrographs of double CMZP coatings of different first and second coatings	21
Figure 9. SEM micrographs of Mg-Al ₂ TiO ₅ coatings under high solution concentration of 2.5 mol/L and lift rate of 6.5 cm/min	24
Figure 10. SEM micrographs of Mg-Al ₂ TiO ₅ coatings under low solution concentration of 0.3 mol/L and lift rate of 6.5 cm/min	26
Figure 11. SEM micrographs of Mg-Al ₂ TiO ₅ coatings under medium solution concentration of 1.2 mol/L and lift rate of 6.5 cm/min	28
Figure 12. SEM micrographs of double Mg-Al ₂ TiO ₅ coatings of different first and second coatings	26
Figure 13. X-ray diffraction patterns of CMZP coating fired in air (a) and CMZP powder (b)	33
Figure 14. X-ray diffraction patterns of CMZP coating fired and isolated from air (a) and CMZP powder (b)	34
Figure 15. X-ray diffraction patterns of CMZP coating fired in an Atmosphere of poor oxygen (a) and CMZP powder	35
Figure 16. X-ray diffraction patterns of CMZP coating fired in an atmosphere of rich CO ₂ (a) and CMZP powder (b)	36
Figure 17. X-ray diffraction patterns of CMZP coating fired in an atmosphere of partial oxygen (a) and CMZP powder (b)	37
Figure 18. X-ray diffraction patterns of Mg-Al ₂ TiO ₅ coating utilizing hydrolyzed solution (a) and Mg-Al ₂ TiO ₅ powder (b)	38
Figure 19. X-ray diffraction patterns of Mg-Al ₂ TiO ₅ coating utilizing unhydrolyzed solution (a) and Mg-Al ₂ TiO ₅ powder (b)	40
Figure 20. Surface microstructure of CMZP coated samples exhibited cracks and small spalling after a thermal shock of 1000°C	41
Figure 21. Surface microstructure of CMZP coated samples exhibited cracks after a thermal shock of 750°C	41
Figure 22. Surface microstructure of CMZP coated samples exhibited no cracks after a thermal shock of 500°C	42
Figure 23. Surface microstructure of Mg-Al ₂ TiO ₅ coated samples exhibited cracks and small spalling after a thermal shock of 1000°C	43
Figure 24. Surface microstructure of Mg-Al ₂ TiO ₅ coated samples exhibited cracks after a thermal shock of 750°C	43

Figure 25. Surface microstructure of Mg-Al ₂ TiO ₅ coated samples exhibited no cracks after a thermal shock of 500°C	44
Figure 26. Weight loss of CMZP coated and uncoated SiC samples after sodium corrosion	46
Figure 27. Flexural strength of CMZP coated and uncoated SiC samples before and after sodium corrosion	46
Figure 28. Corrosion of uncoated SiC samples by sodium carbonate	47
Figure 29. Dense protective layer on surface of CMZP coated SiC samples formed after sodium corrosion	47
Figure 30. Distribution of Ca, Mg, Zr, P, and Si on sample surfaces	48
Figure 31. Weight loss of Mg-Al ₂ TiO ₅ coated and uncoated SiC samples after sodium corrosion	49
Figure 32. Weight loss of Mg-Al ₂ TiO ₅ coated and uncoated SiC samples before and after sodium corrosion	49
Figure 33. Dense protective layer on surface of Mg-Al ₂ TiO ₅ coated SiC samples formed after sodium corrosion	50
Figure 34. Distribution of Al, Ti, and Si on sample surfaces	50
Figure 35. SEM micrographs of uncorroded areas (a) and corroded areas (b) of CMZP coated samples	52
Figure 36. X-ray diffraction of uncorroded areas of CMZP coating (a) and the sample before corrosion test (b)	53
Figure 37. EDX spectrum on a cross-section of the uncorroded areas of the CMZP coating	54
Figure 38. EDX spectrum on a cross-section of the corroded areas of the CMZP coating	54
Figure 39. SEM micrographs of uncorroded areas (a) and corroded areas (b) of the Mg-Al ₂ TiO ₅ coated samples	55
Figure 40. X-ray diffraction of the uncorroded areas of the Mg-Al ₂ TiO ₅ coating (a) and the sample before the corrosion test	56
Figure 41. EDX spectrum on a cross-section of the uncorroded areas of the Mg-Al ₂ TiO ₅ coating	57
Figure 42. EDX spectrum on a cross-section of the corroded areas of the Mg-Al ₂ TiO ₅ coating	57
Figure 43. Surface microstructure of aged CMZP coated samples after a thermal shock of 1000°C	58
Figure 44. Surface microstructure of unaged CMZP coated samples after a thermal shock of 1000°C	59
Figure 45. Surface microstructure of aged CMZP coated samples after a thermal shock of 750°C	59
Figure 46. Surface microstructure of unaged CMZP coated samples after a thermal shock of 750°C	60
Figure 47. Surface microstructure of aged Mg-Al ₂ TiO ₅ coated samples after a thermal shock of 1000°C	61
Figure 48. Surface microstructure of unaged Mg-Al ₂ TiO ₅ coated samples after a thermal shock of 1000°C	61

Figure 49. Surface microstructure of aged Mg-Al ₂ TiO ₅ coated samples after a thermal shock of 750°C	62
Figure 50. Surface microstructure of unaged Mg-Al ₂ TiO ₅ coated samples after a thermal shock of 750°C	62
Figure 51. Weight loss of aged and unaged CMZP coated SiC samples after sodium corrosion	64
Figure 52. Flexural strength of aged and unaged CMZP coated SiC samples before and after sodium corrosion.	64
Figure 53. Distribution of Ca, Mg, Zr, P, and Si on aged CMZP coated sample surfaces	65
Figure 54. Distribution of Ca, Mg, Zr, P, and Si on unaged CMZP coated sample surfaces	65
Figure 55. Weight loss of aged and unaged Mg-Al ₂ TiO ₅ coated SiC samples after sodium corrosion	67
Figure 56. Flexural strength of aged and unaged Mg-Al ₂ TiO ₅ coated SiC samples before and after sodium corrosion	67
Figure 57. Distribution of Mg, Al, Ti, and Si on aged Mg-Al ₂ TiO ₅ coated sample surfaces	68
Figure 58. Distribution of Mg, Al, Ti, and Si on unaged Mg-Al ₂ TiO ₅ coated sample surfaces	69
Figure 59. Acid-catalyzed hydrolysis by electrophilic reaction mechanism	73
Figure 60. Base-catalyzed hydrolysis by nucleophilic reaction mechanism	74
Figure 61. Sol-gel tree	75
Figure 62. Heat treatment schedule for Mg-doped Al ₂ TiO ₅ coatings	80
Figure 63. Heat treatment schedule for CMZP coatings	81
Figure 64. Schematic of the alkali corrosion apparatus used with four-point bending test	82
Figure 65. Schematic of the alkali corrosion apparatus used for the aging test	82
Figure 66. SEM micrograph of a fractured surface for a surface-treated Si ₃ N ₄ and corresponding elemental mappings	84
Figure 67. XRD patterns of a) CMZP calcined powder, b) Mg-doped Al ₂ TiO ₅ calcined powder	86
Figure 68. SEM micrograph of CMZP coating	87
Figure 69. SEM micrograph of a fractured surface for Si ₃ N ₄ coated with CMZP and corresponding elemental mappings	88
Figure 70. SEM micrograph of Mg-doped Al ₂ TiO ₅ coating	89
Figure 71. Surface of microstructure of a) CMZP and b) Mg-doped Al ₂ TiO ₅ after thermal shock test at 800°C	91
Figure 72. EDX spectrum of CMZP coatings a) before corrosion b) after corrosion	93
Figure 73a. SEM micrograph of CMZP coating after corrosion	94
Figure 73b. EDX elemental mapping for CMZP coating after corrosion	95
Figure 74. SEM micrographs of the corrosion scale obtained after water leach for a) uncoated Si ₃ N ₄ , and b) Si ₃ N ₄ coated originally with CMZP	97

Figure 75. SEM micrographs of the attack morphology obtained after mild HF (15 min, 10% HF, 60°C) treatment	98
Figure 76. SEM micrograph of the corrosion product layer and associated elemental maps for Si₃N₄ coated with Mg-doped Al₂TiO₅ and corroded at 1000°C for 48 h in an NaNO₃ containing atmosphere	99
Figure 77. SEM micrograph of the attacked microstructure obtained after water leach and mild HF treatment for Si₃N₄ coated with Mg-doped Al₂TiO₅ and corroded at 1000°C for 48 h in an NaNO₃ containing atmosphere	100
Figure 78. Fractography and corresponding EDX mappings of as-received Si₃N₄ after 96-hour corrosion at 1000°C	102
Figure 79. Fractography and corresponding EDX mappings of as-received Si₃N₄ coated with CMZP after 96-hour corrosion at 1000°C	103
Figure 80. Fractography and corresponding EDX mapping of Si₃N₄ coated with Mg-doped Al₂TiO₅ after 96-hour corrosion at 1000°C	104
Figure 81. Four-point bending fractural strength of coated and uncoated Si₃N₄ before and after 96-hour corrosion at 1000°C	105
Figure 82. Three-point bending flexural strength as a function of time after sodium vapor corrosion at 1000°C	107
Figure 83. Weight loss measurements as a function of time after sodium vapor corrosion at 1000°C	107

List of Tables

Table 1.	Properties of the Illinois No. 6 Coal	12
Table 2.	Comparison of CMZP coatings under different solution Concentrations and lift rates	13
Table 3.	Comparison of single and double CMZP coatings	20
Table 4.	Comparison of different Mg-Al ₂ TiO ₅ coatings under different solution concentrations and lift rates	23
Table 5.	Comparison of single and different double Mg-Al ₂ TiO ₅ coatings	23
Table 6.	Comparison of different CMZP coatings under different firing Atmospheres	32
Table 7.	Thermal shock resistance of CMZP coated SiC samples	39
Table 8.	Thermal shock resistance of Mg-Al ₂ TiO ₅ coated SiC samples	42
Table 9.	Weight loss of CMZP coated and uncoated samples after sodium corrosion (%)	44
Table 10.	Flexural strength of CMZP coated and uncoated SiC samples before and after sodium corrosion (MPa)	45
Table 11.	Weight loss of Mg-Al ₂ TiO ₅ coated and uncoated samples after sodium corrosion (%)	48
Table 12.	Flexural strength of Mg-Al ₂ TiO ₅ coated and uncoated SiC samples Before and after sodium corrosion (MPa)	48
Table 13.	Thermal shock resistance of aged and unaged CMZP coated SiC samples	58
Table 14.	Thermal shock resistance of aged and unaged Mg-Al ₂ TiO ₅ coated SiC samples	60
Table 15.	Weight loss of aged and unaged CMZP coated SiC samples after sodium corrosion (%)	63
Table 16.	Flexural strength of aged and unaged CMZP coated SiC samples before and after sodium corrosion (MPa)	63
Table 17.	Distribution of Ca, Mg, Zr, P, and Si on sample surfaces after sodium corrosion at 1000°C (%)	66
Table 18.	Weight loss of aged and unaged Mg-Al ₂ TiO ₅ coated SiC samples after sodium corrosion (%)	66
Table 19.	Flexural strength of aged and unaged Mg-Al ₂ TiO ₅ coated SiC samples before and after sodium corrosion (MPa)	66
Table 20.	Distribution of Mg, Al, Ti, and Si on the sample surfaces after the sodium corrosion at 1000°C (%)	68
Table 21.	Contact angle for as-received Si ₃ N ₄ and Si ₃ N ₄ surface treated for CMZP and Mg-doped Al ₂ TiO ₅	83
Table 22.	Thermal shock resistance of coated and uncoated Si ₃ N ₄ samples	90
Table 23.	Possible phases present in the corrosion product layer	92
Table 24.	Alkali corrosion resistance of coatings	105

Part 1 Development of Coatings for SiC and Si₃N₄

Introduction

Silicon carbide is a promising candidate for a variety of high temperature structural applications because of its high thermal shock resistance, high thermal conductivity, low thermal expansion, high fracture toughness, creep resistance, and corrosive resistance in air. The shortcoming of this material is its instability in the presence of oxygen at high temperature.

High temperature alkali corrosion has been known to cause premature failure of ceramic components used in advanced high temperature coal combustion systems such as coal gasification and clean-up, coal fire gas turbines, and high efficiency heat engines. The non-oxide ceramics, such as SiC, are applied in these systems for their well-known and desirable high temperature thermal and mechanical properties. However, these materials are prone to rapid corrosion under high temperature coal combustion conditions.

In the past several years, new high temperature, low thermal expansion materials such as (Ca_{0.6}Mg_{0.4})Zr₄(PO₄)₆ (CMZP) and Mg-doped Al₂TiO₅ (Mg-Al₂TiO₅) have been developed.¹⁻⁶ These materials have been produced with near zero bulk thermal expansion and low crystal anisotropy, very low thermal conductivity, thermal stability up to 1500°C, excellent thermal shock resistance, and good corrosion resistance to alkali attack.

Li et al.⁷ coated CMZP on silicon carbide (SiC) and silicon nitride (Si₃N₄) substrates using sol-gel techniques. The coatings exhibited good thermal shock resistance and greatly improved the alkali corrosion resistance of SiC and Si₃N₄ substrates. Brown et al.⁸ have developed a method of sol-gel coating Mg-doped Al₂TiO₅ material that is stable at low temperatures. Kang⁹ used Mg-Al₂TiO₅ and CMZP to coat porous SiC filters, resulting in a significant improvement of the alkali corrosion resistance of the SiC samples.

The objective of this research is to apply CMZP and Mg-Al₂TiO₅ as coatings to SiC in an attempt to improve its alkali corrosion resistance under coal combustion atmospheres as well as improve its high temperature mechanical properties. The research will not only develop and characterize CMZP and Mg-Al₂TiO₅ coatings but will also strive to expand the existing knowledge of the mechanism of coal combustion corrosion of SiC in the temperature range of 1000-1400°C.

Literature Review

Silicon Carbide

SiC is one of the promising candidates for a variety of high temperature structural applications because of its high temperature shock resistance, high thermal conductivity, low thermal expansion, high fracture toughness, creep resistance, and corrosion resistance in air.¹⁰⁻¹² This material is unstable in the presence of oxygen at high temperatures and exhibits either active or passive oxidation depending on the partial pressure of oxygen.

In the presence of low oxygen partial pressure, the active oxidation of silicon carbide occurs, resulting in the formation of SiO gas.¹³⁻¹⁷ In the presence of higher oxygen partial pressure, passive oxidation occurs, resulting in a thin, self-healing, passive SiO₂ scale on all exposed surfaces of silicon carbide.¹⁸⁻²⁹

The oxidation of SiC is governed by oxygen transport through the silica layer. The oxidation is greatly accelerated when the protective scale, silica layer reacts with the alkali. The alkali corrosion in this case can be envisioned as a continuous dissolution-oxidation process in which the oxide layer is readily dissolved in the alkali to form an alkali silicate melt, while oxygen diffuses through the liquid to oxidize the underlying carbide.^{30,31}

Some authors have studied the oxidation of SiC in wet O₂ or H₂O and pointed out that the oxidation rate is much higher than in an atmosphere without water vapor.³²⁻³⁸ Water vapor is an oxidizing agent for SiC. The rate of oxidation is accelerated when water vapor is added to oxygen, and possibly water vapor is accelerating the diffusion of oxygen, carbon monoxide, or carbon dioxide through the layer of SiO₂, or water vapor promoting the transition of amorphous silica to cristobalite might account for the accelerated rate.

Many authors have investigated the alkali corrosion behavior of SiC. Horn³⁹ reported dislocation etch pitting at 1000°C and Amelincks et al.⁴⁰ and Buchner et al.⁴¹ pointed to complete dissolution at temperatures less than 900°C. McKee et al.⁴² studied both salt immersion and thin film deposition of sodium sulfate and sodium carbonate on β-SiC and reported active corrosion by deep basic melts with carbon added. When SiC specimens coated with sodium sulfate were exposed to air at 1000°C, the sodium sulfate decomposed and the SiC became corroded. Buchner et al.⁴¹ also pointed out the bubble formation and devitrification of protective silica scales were observed upon examination of the morphology of corrosion products deposited on the SiC substrate. Jacobson et al.⁴³ deposited a thin film of molten sodium sulfate and sodium carbonate to corrode sintered SiC at 1000°C. They found that these films lead to glassy products on the SiC surface after 48 hours at 1000°C. These products contained small amounts of sodium silicate and 10 to 20 times the amount of silica. The attack produced pitting due to gas evolution and grain boundary etching. It was found that the corrosive attack led to a 32% decrease in strength of SiC. Kim et al.⁴⁴ pointed out that the room temperature flexural strength of sintered SiC was reduced by up to 50% when exposed for 10 hours at 1400°C to H₂-H₂O atmosphere, and up to 40% when similarly exposed to O₂-Ar atmosphere.

(Ca_{0.6}Mg_{0.4})Zr₄(PO₄)₆ (CMZP)

CMZP is one of the sodium zirconium phosphate (NaZr₂(PO₄)₃ or NZP type materials characterized with an open structure and ability to allow other ions to replace Na⁺ and/or P⁺⁵ cations forming new compounds.⁴⁵ Hong⁴⁶ and Goodenough et al.⁴⁷ reported on Na_{1+x}Zr₂Si_xP_{3-x}O₁₂ (NASICON) and proposed the substitution of β-Al₂O₃ used in high temperature batteries for industrial solid-state electrolyte applications. Some other authors⁴⁸⁻⁵⁰ studied the ion conductivity of some NZP type materials and the structure.

Since it was found that some NASICON compounds exhibited low thermal expansion, the studies were focused on the development of new NZP type materials with a low thermal

expansion. The driving force for developing low expansion ceramics was a desire to find potential high temperature structural materials with a high thermal shock resistance.

Brown et al.⁵¹ studied $(\text{Ca}_{1-x}\text{Mg}_x)\text{Zr}_4(\text{PO}_4)_6$ compounds with x less than or equal to 0.4 and pointed out that at $x = 0.4$, the compound $(\text{Ca}_{0.6}\text{Mg}_{0.4})\text{Zr}_4(\text{PO}_4)_6$ (CMZP) exhibited the lowest thermal expansion, low bulk coefficient of thermal expansion, low thermal conductivity, excellent thermal shock resistance, good corrosion resistance to alkali attack, and stability up to 1500°C.

Li et al.⁷ investigated thin film coatings of CMZP on SiC and Si_3N_4 substrates utilizing sol-gel coating techniques. The CMZP coatings exhibited good thermal shock resistance and greatly improved alkali corrosion resistance of SiC and Si_3N_4 .

Kang⁹ studied alkali/steam corrosion resistance of commercial SiC products coated with sol-gel deposited CMZP. It was pointed out that in high temperature, high pressure (HTHP) environments, CMZP coatings improved the thermal shock resistance, corrosion resistance, and mechanical properties of SiC substrates.

Aluminum Titanate

Al_2TiO_5 is being considered for use in many high temperature structural applications because of its well known high temperature, low thermal expansion properties, which result in good thermal shock resistance.

Al_2TiO_5 was selected for vehicle engine components testing for its thermal insulation and higher exhaust temperature, and the testing was completed without engine failure.^{52,53} Several researchers developed aluminum titanate composites to increase the strength⁵⁴ or improve microcracking.⁵⁵

Brown et al.⁸ have developed sol-gel coating techniques for an Mg-doped Al_2TiO_5 material. Kang⁹ investigated the effects of high temperature, high pressure, steam/alkali environments on the corrosion resistance of SiC coated with Al_2TiO_5 . It was pointed out that the Al_2TiO_5 coatings significantly improved the alkali corrosion resistance of the SiC as compared to the uncoated material.

Sol-Gel Techniques

In recent years, sol-gel processing has been an important technique for coating a variety of metallic or ceramic substrates to improve the corrosion resistance, wear resistance, and electrical and optical properties. The advantages of sol-gel coating techniques are attractive, especially for purity and homogeneity of the molecular level, although they involve high costs and long processing time.⁵⁶

The sol-gel techniques involve two key steps:

hydrolysis, $\text{M}(\text{OH})_x + \text{H}_2\text{O} \rightarrow \text{M}(\text{OR})_{x-1}\text{OH} + \text{ROH}$, and

condensation-polymerization, $2\text{M(OR)}_{x-1}\text{OH} \rightarrow \text{H}_2\text{O} + (\text{OR})_{x-1}\text{M-O-M(OR)}_{x-1}$

where M is a metal species (Si, Al, Ti, Zr, etc.) and R is an organic group (methyl, ethyl, isopropyl, etc.).⁵⁷

Experimental Procedures

Substrate Pre-Treatment

The SiC substrates used in the study were prepared by cutting commercial grade SiC plate into 8x10x50 mm pieces. The substrates used for the 100-hour slagging combustion test were cut into 8x25x155 mm shapes. In order to prepare crack-free coatings and enhance the adhesion of coating to substrate, the substrates were treated to form an oxide layer or groups.

The samples to be coated with CMZP were first washed with deionized water for 30 minutes in a solid state/ultrasonic cleaner, then soaked in acetone for 1 hour, and dried at 110°C for 2 hours. Next, the samples were washed with 10% HF solution, rinsed with deionized water, dried at 110°C for 2 hours, and calcined at 1200°C for 6 hours. Finally, the calcined samples were washed with 10% HCl solution, rinsed with deionized water, and dried at 110°C for 2 hours.

The samples to be coated with Mg-Al₂TiO₅ were first washed with deionized water for 30 minutes in a solid state/ultrasonic cleaner, then soaked in 1:1 HNO₃ solution for 6 hours, washed with deionized water, dried at 110°C for 2 hours, and calcined at 1200°C for 6 hours. Finally, the calcined samples were washed with 10% HCl solution, rinsed with deionized water, and dried at 110°C for 2 hours.

Preparation of CMZP Solution

The precursors for CMZP solution are calcium chloride (CaCl₂), magnesium perchlorate hexahydrate (Mg(ClO₄)₂·6H₂O), zirconium propoxide (Zr(C₃H₇O)₄), Triethyl phosphate ((C₂H₅O)₃P(O)), and hydrochloric acid (HCl). The stoichiometric amounts of calcium chloride and magnesium perchlorate hexahydrate were mixed in ethyl alcohol. The mixture was constantly stirred while hydrochloric acid was added drop by drop until a pH of between 2.2 and 4.0 was reached, then zirconium propoxide and triethyl phosphate were added drop by drop. The concentration of the CMZP solution was 0.1 mol/L and the solution was clear with a slight yellow color.

Preparation of Mg-Al₂TiO₅ Solution

The precursors for Mg-Al₂TiO₅ solution are magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O), aluminum tri-sec butoxide (Al[C₂H₅CH(CH₃CH₃)O]₃), titanium butoxide (Ti[CH₃(CH₂)₃O]₄) and nitric acid (HNO₃). The stoichiometric amounts of magnesium nitrate hexahydrate, aluminum tri-sec butoxide, and titanium butoxide were first weighted and homogenized by stirring. A solution of ethyl alcohol and nitric acid with a resultant pH between 1.0 and 4.5 was added drop by drop to the mixture of the magnesium, aluminum, and titanium precursors under constant stirring conditions. The concentration of the Mg_{0.1}Al_{1.8}Ti_{1.1}O₅ solution was 1.2 mol/L. The solution was clear with a slight green color.

Coating Techniques

CMZP Coating

The pre-treated samples were soaked in boiling CMZP solution for 30 minutes and remained in the solution while it was cooled slowly to room temperature. The samples were withdrawn at a rate of 4-8 cm/min at room temperature. The coated samples were cured at room temperature for 72 hours at a relative humidity of 40-80%, then air-dried at room temperature for an additional 72 hours and dried at 40-60°C for 48 hours, then finally heat treated at 400°C in air for 6 hours. The rates of increasing and decreasing the temperature were 1°C/min and 5°C/min, respectively.

The second coating was applied following the same procedure used for the first coating. In order to obtain the pure CMZP phase, the samples were fired in covered crucibles fully filled with CMZP powder at 1200°C for 24 hours. The rates of increasing temperature were 1°C/min and 5°C/min, respectively, before and after 400°C, while the rate of decreasing temperature from 1200°C to room temperature was 5°C/min. Figure 1 shows the heat treatment schedule for CMZP coatings on dense SiC.

Mg-Al₂TiO₅ Coating

The pre-treated samples were immersed in the Mg-Al₂TiO₅ solution and vibrated for 30 minutes. The samples were withdrawn at a rate of 4-8 cm/min. The coated samples were put in a container with saturated humidity for 72 hours. Next, the samples were dried at room temperature in air for 24 hours, then dried at 65°C for 24 hours. Finally, the samples were fired at 400°C in air for 6 hours. The rates of increasing and decreasing temperature were 1°C/min and 5°C/min, respectively.

The second coating was applied following the same procedure used for the first coating. The coated samples were fired at 1300°C in air for 10 hours. The rates of increasing temperature were 1°C/min and 5°C/min, respectively, before and after 400°C, while the rate of decreasing temperature from 1300°C to room temperature was 5°C/min. Figure 2 shows the heat treatment schedule for Mg-Al₂TiO₅ coatings on dense SiC.

Thermal Shock Resistance Test

The thermal shock resistance of CMZP coated samples was investigated. Four groups of samples were heated to 300, 500, 750, and 1000°C, respectively, and then quenched in water at room temperature (25°C). The surface microstructure of coatings and adhesion between the coatings and substrates were examined by SEM and EDX. An Environmental Scanning Electron Microscope E-3 was used.

Four groups of samples coated with Mg-Al₂TiO₅ were heated to 300, 500, 750, and 1000°C, respectively, and then quenched in water at room temperature (25°C). The surface microstructure of coatings and adhesion between the coatings and substrates were examined by SEM and EDX.

First coating: room temperature

↓ 1°C/min

400°C, for 6 hours

↓ 5°C/min

room temperature

Second coating: room temperature

↓ 1°C/min

400°C, for 6 hours

↓ 5°C/min

1200°C, for 24 hours

↓ 5°C/min

room temperature

Figure 1. Heat treatment schedule for CMZP coating dense SiC

Figure 2. Heat treatment schedule for Mg-Al₂TiO₅ coating dense SiC

Alkali Corrosion Resistance Test

The alkali corrosion resistance of both uncoated and CMZP-coated SiC samples was examined by determining the weight loss and flexural strength degradation of samples exposed to molten Na_2CO_3 and an atmosphere containing sodium. Weighed samples were heated to 200°C , then dipped into a saturated solution of Na_2CO_3 to obtain a thin layer of Na_2CO_3 on the surface. The sodium-coated samples were heated in a sodium atmosphere at 900, 1000, and 1100°C , respectively, for 48 hours.

The crucible containing Na_2CO_3 was weighed before and after each run to determine the amount of weight loss of the Na_2CO_3 during the corrosion time interval. Assuming the vapors behave like ideal gasses and using the data from the weight loss and volume of the furnace tube, the alkali vapor concentration was calculated to be approximately 5 vol %. To determine the weight loss after the exposure, the samples were rinsed in acetone and washed in distilled water at 100°C to remove any physically absorbed salt and sodium silicates. Any glass which formed on the surface of the samples was then dissolved in dilute HF acid. The etching was repeated until no noticeable difference in weight change was detected.

The room temperature flexural strength of both as-received and corroded SiC samples was determined by 4-point bending using an ATS Test System. To decrease the effect of random errors, the average strength of every group is reported.

The microstructure and fracture surfaces of the samples before and after corrosion were examined by EDX and the phases of sample surfaces before and after corrosion were identified using XRD.

The alkali corrosion testing of $\text{Mg-Al}_2\text{TiO}_5$ coatings follows the same procedures for CMZP coatings as described previously.

100-Hour Slagging Combustion Test

The SiC samples coated with CMZP and $\text{Mg-Al}_2\text{TiO}_5$, respectively, and uncoated samples were tested in a 100-hour slagging combustion test at the Energy and Environmental Research Center at the University of North Dakota, in June 1995, as part of the Combustion 2000 project. The objective of this test was to examine CMZP and $\text{Mg-Al}_2\text{TiO}_5$ coated SiC samples for improvement in corrosion resistance under coal combustion atmospheres at 1350 - 1400°C for 100 hours.

Coating Procedure

a) Substrate Pre-Treatment. The SiC samples ($8 \times 25 \times 155$ mm) to be coated with CMZP were first washed with deionized water for 30 minutes in a solid state/ultrasonic cleaner, then soaked in acetone for 1 hour, and dried at 100°C for 2 hours. Next, the samples were washed with 10% HF solution, rinsed with deionized water, dried at 100°C for 2 hours, and calcined at 1200°C for 6 hours. Finally the calcined samples were washed in 10% HCl solution, rinsed with deionized water, and dried at 100°C for 2 hours.

The samples to be coated with $\text{Mg-Al}_2\text{TiO}_5$ were first washed with deionized water for 30 minutes in a solid state/ultrasonic cleaner, then soaked in 1:1 HNO_3 solution for 6 hours, washed with deionized water, dried at 100°C for 2 hours, and calcined at 1200°C for 6 hours. Finally, the calcined samples were washed in 10% HCl solution, rinsed with deionized water, and dried at 100°C for 2 hours.

b) Preparation of Solution. The precursors for CMZP solution are CaCl_2 , $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zr}(\text{C}_3\text{H}_7\text{O})_4$, and $(\text{C}_2\text{H}_5\text{O})_3\text{P}(\text{O})$. The stoichiometric amounts of CaCl_2 and $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ were mixed in ethyl alcohol. The mixture was constantly stirred while HCl was added until a pH between 2.0 and 4.0 was reached. Then $\text{Zr}(\text{C}_3\text{H}_7\text{O})_4$, and $(\text{C}_2\text{H}_5\text{O})_3\text{P}(\text{O})$ were added drop by drop. The concentration of CMZP solution was 0.1 mol/L, while the corresponding lift rate of the samples was 6.5 cm/min.

The precursors for $\text{Mg-Al}_2\text{TiO}_5$ solution are $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}[\text{C}_2\text{H}_5\text{CH}(\text{CH}_3\text{CH})\text{O}]_3$, and $\text{Ti}[\text{CH}_3(\text{CH}_2)_3\text{O}]_4$. The stoichiometric amounts of these precursors were first weighed and homogenized by stirring. A solution of ethyl alcohol and HNO_3 solution with resultant pH between 1.0 and 4.5 was added drop by drop to the mixture. The concentration was 1.2 mol/L, while the corresponding lift rate of the samples was 6.5 cm/min.

c) Coating Techniques. The pre-treated samples were soaked in boiling CMZP solution for 30 minutes and remained in the solution while it cooled slowly to room temperature. The samples were withdrawn at a rate of 6.5 cm/min at room temperature. The coated samples were cured at room temperature for 72 hours at a relative humidity of 40-80%, then air-dried at room temperature for an additional 72 hours and dried at $40\text{-}60^\circ\text{C}$ for 48 hours, then finally heat treated at 400°C in air for 6 hours. The rates of increasing and decreasing the temperature were 1°C and 5°C , respectively. The second coating was applied following the same procedure of the first coating. In order to obtain the pure CMZP phase, the samples were fired in large covered crucibles fully lined with CMZP powder at 1200°C for 24 hours. The rates of increasing temperature were $1^\circ\text{C}/\text{min}$ and $5^\circ\text{C}/\text{min}$, respectively, before and after 400°C , while the rate of decreasing temperature from 1200°C to room temperature was $5^\circ\text{C}/\text{min}$.

The pre-treated samples were immersed in the unhydrolyzed $\text{Mg-Al}_2\text{TiO}_5$ solution and vibrated for 30 minutes. The dip coating withdrawing rate was 6.5 cm/min. Then the samples were placed in a container with saturated humidity for 72 hours. Next, the samples were dried at 65°C for 12 hours. Finally, the samples were fired at 400°C in air for 6 hours. The rates of increasing and decreasing temperature were $1^\circ\text{C}/\text{min}$ and $5^\circ\text{C}/\text{min}$, respectively. The second coating was applied following the same procedures used for the first coating. The coated samples were fired at 1300°C in air for 10 hours. The rates of increasing temperature were $1^\circ\text{C}/\text{min}$ and $5^\circ\text{C}/\text{min}$, respectively, before and after 400°C , while the rate of decreasing temperature from 1300°C to room temperature was $2^\circ\text{C}/\text{min}$.

The Test Conditions

The samples labeled with an R-prefix, including CMZP and $\text{Mg-Al}_2\text{TiO}_5$ coated and uncoated samples, were embedded in the refractory wall of the main combustor near the furnace exit and cemented in place with zircar alumina cement. The samples labeled with a Cl-prefix were

embedded just downstream of the Probe Bank One. Figure 3 shows the isometric drawing of the combustion test system. The samples were exposed for the entire length of the test.

When the furnace exit temperature had achieved 1315°C, firing natural gas since the unit started, problems were encountered with the coal feeder. When the coal feeder was operating and coal firing was initiated, the unit was fired with natural gas and a furnace exit temperature above 1200°C was maintained for approximately 52 hours. Therefore, all samples were exposed to natural gas at these elevated temperatures for 52 hours followed by 95-100 hours of coal firing. The radiant zone samples were exposed for the full test period, approximately 52 hours of gas firing followed by 95-100 hours of coal firing. After exposure, slag and ash buildup on the samples was excessive and cemented the samples to the duct. Samples with a Cl-prefix had to be removed with an air hammer. Most of the samples were broken in this removal process.

During coal firing, the test furnace was fired at 750,000 Btu/hr, achieving a furnace exit gas temperature between 1340 and 1370°C using 15% excess air. Due to excessive slag formation in the refractory lined ductwork at the furnace exit, the system was shut down periodically for cleaning. After cleaning, the system was brought back up to operating temperature using natural gas prior to switching to coal. The Illinois No. 6 coal was used for testing, which analyses are provided in Table 1.

Measurements of the Samples

The XRD patterns of the samples coated with CMZP and Mg-Al₂TiO₅ were determined. Before the measurement, all loose slag was removed from the samples.

The microstructure of the surface of the samples coated with CMZP and Mg-Al₂TiO₅ was examined by SEM. The EDX analysis on the cross-section of the samples coated with CMZP and Mg-Al₂TiO₅ was done.

Aging Process

An aging process was utilized to improve the quality of the CMZP and Mg-Al₂TiO₅ coated samples. This aging process is described below.

The CMZP coated samples were fired in large covered crucibles fully filled with CMZP powder at 1200°C for 100 hours. The cover was sealed with liquid K₂SiO₃. This technique results in an atmosphere which is nearly oxygen free.

The Mg-Al₂TiO₅ coated samples were fired in air at 1300°C for 100 hours.

Figure 3. Isometric drawing of the combustion test system

Table 1. Properties of the Illinois No. 6 Coal

Test Number:	AF-CTS-711	
Date Sampled:	3/14/95	
Sample Number:	95-0254	
Proximate Analysis, %	As-Fired	Moisture-Free
Moisture	6.30	—
Volatile Matter	39.31	41.96
Fixed Carbon	43.95	46.89
Ash	10.45	11.15
Ultimate Analysis, %		
Hydrogen	5.04	4.63
Carbon	65.55	69.97
Nitrogen	1.24	1.33
Sulfur	3.24	3.46
Oxygen	14.49	9.47
Ash	10.45	11.15
Moisture	6.30	—
Heating Value, Btu/lb	11,676	12,464
Sulfur Input, lb SO ₂ /MMBtu	5.55	
Ash Input, lb/MMBtu	8.95	
Sieve Analysis	Sieve Mesh No.	Retained, wt%
	100	4.50
	140	10.88
	200	12.38
	230	7.69
	270	6.38
	325	8.44
	<325	49.72
% by Weight < 200 Mesh		72.23
Ash Analysis, wt%	% by Weight	% SO ₃ -Free
SiO ₂	48.20	49.65
Al ₂ O ₃	18.51	19.07
Fe ₂ O ₃	18.01	18.56
TiO ₂	0.77	0.80
P ₂ O ₅	0.54	0.55
CaO	4.65	4.79
MgO	1.15	1.18
Na ₂ O	3.55	3.65
K ₂ O	1.70	1.75
SO ₃	2.92	—
Total	85.49	91.08
Ash Fusion Temperature, °F	Oxidizing	Reducing
Initial Deformation	2307	2047
Softening	2359	2192
Hemispherical	2409	2213
Fluid	2532	2324

Results and Discussion

Characterization of Coatings on SiC

CMZP Coatings

In order to obtain dense, homogeneous and crack-free CMZP coatings, the influence of the solution concentration and the lift rate of the samples were investigated. It was found that the quality of the CMZP coatings is strongly dependent on the solution concentration and lift rate. High concentration and fast lift rate resulted in cracking of the coating during subsequent heat treatment. For forming crack-free coatings, the concentration of the CMZP solutions needs to be kept between 0.05 and 0.2 mol/L, while the lift rate stays between 4.3 and 8.1 cm/min. It was found that the high solution concentration made the coatings thick and inhomogeneous with holes and cracks, while low solution concentration made the coatings too thin, especially in the upper part of the samples due to the influence of gravity.

Figure 4 shows the SEM micrographs of the as-received SiC sample: (a) grains and holes on the sample surface, (b) the interior surface of a hole. Clearly, coatings must not only cover the surface of grains but also cover the interior surface of the holds. Figure 5 shows the SEM micrographs of CMZP coatings under the high solution concentration of 0.2 mol/L and lift rate of 6.5 cm/min. Figure 6 shows the SEM micrographs of CMZP coatings under low solution concentration of 0.05 mol/L and lift rate of 6.5 cm/min. Figure 7 shows the SEM micrographs of CMZP coatings under the medium solution concentration of 0.1 mol/L and lift rate of 6.5/min. Table 2 shows the comparison of different coatings under different solution concentrations and lift rates.

Table 2. Comparison of CMZP coatings under different solution concentrations and lift rates

Solution Concentration (mol/L)	Lift Rate (cm/min)	Grain Surface	Interior Surface
0.02	4 - 8	thin	thin
0.05	4 - 8	thin	thin
0.10	4 - 8	good	good
0.15	4 - 8	better	better
0.20	4 - 8	thicker, little cracks	cracks
0.25	4 - 8	thick, cracks	many cracks

(a)

(b)

Figure 4. SEM micrographs of as-received SiC samples: (a) grains and holes on the sample surface; (b) interior surface of a hole

(a)

(b)

Figure 5. SEM micrographs of CMZP coatings under the high solution concentration of 0.2 mol/L and lift rate of 6.5 cm/min: (a) grains on sample surface; (b) surface of a grain

(c)

Figure 5 cont'd. SEM micrographs of CMZP coatings under the high solution concentration of 0.2 mol/L and lift rate of 6.5 cm/min: (c) interior surface of a hole

(a)

(b)

Figure 6. SEM micrographs of CMZP coatings under the low solution concentration of 0.05 mol/L and lift rate of 6.5 cm/min: (a) grains on the sample surface; (b) surface of a grain

(c)

Figure 6 cont'd. SEM micrographs of CMZP coatings under the low solution concentration of 0.05 mol/L and lift rate of 6.5 cm/min: (c) interior surface of a hole

(a)

(b)

Figure 7. SEM micrographs of CMZP coatings under the medium solution concentration of 0.1 mol/L and lift rate of 6.5 cm/min: (a) grains on the sample surface; (b) surface of a grain

(c)

Figure 7 cont'd. SEM micrographs of CMZP coatings under the medium solution concentration of 0.1 mol/L and lift rate of 6.5 cm/min: (c) interior surface of a hole

It was found that double coating can improve the quality of the coatings, especially decreasing the cracks. Comparison of the results of single and double coatings shows that double coatings are homogeneous and have fewer cracks.

It was found that the different thickness of the first and second coating also influences the quality of the coatings. Figure 8 shows the SEM micrographs of double CMZP coatings of different first and second coatings: (a) the thickness of first and second coatings is 6 μm and 2 μm , respectively; (b) the thickness of first and second coatings is 4 μm ; (c) the thickness of first and second coatings is 2 μm and 6 μm , respectively. The results indicate (c) is better. The most likely reason for this is that CMZP adheres more readily to the layer of CMZP than to the surface of SiC. Table 3 shows the comparison of single and double coatings of CMZP.

Table 3. Comparison of single and double CMZP coatings

	Total Thickness (μm)	Thickness of First Coating (μm)	Thickness of Second Coating (μm)	Quality of Coating
Single Coating	8			worse
Double Coating	8	6	2	better
Double Coating	8	4	4	better
Double Coating	8	2	6	good

(a)

(b)

Figure 8. SEM micrographs of double CMZP coatings of different first and second coatings: (a) thickness of first and second coatings is 6 μm and 2 μm , respectively; (b) thickness of first and second coatings is 4 μm

(c)

Figure 8 cont'd. SEM micrographs of double CMZP coatings of different first and second coatings: (c) thickness of first and second coatings is 2 μm and 6 μm , respectively

Mg-Al₂TiO₅ Coatings

It was found that the quality of Mg-Al₂TiO₅ coatings is strongly dependent on the solution concentration and lift rate. Similar to CMZP coatings, high concentration and fast lift rate resulted in cracking of the coatings during subsequent heat treatment. The solution concentration needs to be kept between 0.3 and 2.5 mol/L, while the lift rates are kept between 4 and 8 cm/min. It was found that coatings formed using a high solution concentration were thick and had holes and cracks, while low solution concentration coatings were too thin, especially in the upper end of samples, from the influence of gravity.

Figure 9 shows the SEM micrographs of Mg-Al₂TiO₅ coatings under the high solution concentration of 2.5 mol/L and lift rate of 6.5 cm/min. Figure 10 shows the SEM micrographs of Mg-Al₂TiO₅ coatings under the low solution concentration of 0.3 mol/L and lift rate of 6.5 cm/min. Figure 11 shows the SEM micrographs of Mg-Al₂TiO₅ coatings under the medium solution concentration of 1.2 mol/L and lift rate of 6.5 cm/min. Table 4 shows the comparison of different coatings under different solution concentrations and lift rates.

Table 4. Comparison of different Mg-Al₂TiO₅ coatings under different solution concentrations and lift rates

Solution Concentration (mol/L)	Lift Rate (cm/min)	Grain surface	Interior Surface
0.3	6.5	too thin	too thin
0.6	6.5	thin	thin
0.9	6.5	better	better
1.2	6.5	good	good
1.5	6.5	better	better
1.8	6.5	thick	thick
2.1	6.5	too thick	too thick
2.5	6.5	too thick	too thick

It was found that double coatings can improve the quality of the coatings. Comparison of the results of single and double coatings shows that double coatings are homogeneous and have fewer cracks. It was found that the quality of double coatings was influenced by different thicknesses of first and second coatings. Figure 12 shows the SEM micrographs of double Mg-Al₂TiO₅ coatings of different first and second coatings (a) the thickness of first and second coatings is 6 μm and 2 μm, respectively; (b) the thickness of first and second coatings is 4 μm; (c) the thickness of first and second coatings is 2 μm and 6 μm, respectively. The results indicated (c) is better. The most likely reason for this is that, like CMZP coatings, Mg-Al₂TiO₅ adheres more readily to the layer of Mg-Al₂TiO₅ than to the surface of SiC. Table 5 shows the comparison of single coatings and different double coatings.

Table 5. Comparison of single and different double Mg-Al₂TiO₅ coatings

	Total Thickness (μm)	Thickness of First Coating (μm)	Thickness of Second Coating (μm)	Quality of Coating
Single Coating	8			worse
Double Coating	8	6	2	better
Double Coating	8	4	4	better
Double Coating	8	2	6	good

(a)

(b)

Figure 9. SEM micrographs of $\text{Mg-Al}_2\text{TiO}_5$ coatings under the high solution concentration of 2.5 mol/L and lift rate of 6.5 cm/min: (a) grains on the sample surface; (b) surface of a grain

(c)

Figure 9 cont'd. SEM micrographs of Mg-Al₂TiO₅ coatings under the high solution concentration of 2.5 mol/L and lift rate of 6.5 cm/min: (c) interior surface of a hole

(a)

(b)

Figure 10. SEM micrographs of $\text{Mg-Al}_2\text{TiO}_5$ coatings under the low solution concentration of 0.3 mol/L and lift rate of 6.5 cm/min: (a) grains on the sample surface; (b) surface of a grain

(c)

Figure 10 cont'd. SEM micrographs of $\text{Mg-Al}_2\text{TiO}_5$ coatings under the low solution concentration of 0.3 mol/L and lift rate of 6.5 cm/min: (c) interior surface of a hole

(a)

(b)

Figure 11. SEM micrographs of $\text{Mg-Al}_2\text{TiO}_5$ coatings under the medium solution concentration of 1.2 mol/L and lift rate of 6.5 cm/min: (a) grains on the sample surface; (b) surface of a grain

(c)

Figure 11 cont'd. SEM micrographs of $\text{Mg-Al}_2\text{TiO}_5$ coatings under the medium solution concentration of 1.2 mol/L and lift rate of 6.5 cm/min:
(c) interior surface of a hole

(a)

(b)

Figure 12. SEM micrographs of double $\text{Mg-Al}_2\text{TiO}_5$ coatings of different first and second coatings: (a) thickness of first and second coatings is $6\text{ }\mu\text{m}$ and $2\text{ }\mu\text{m}$, respectively; (b) thickness of first and second coatings is $4\text{ }\mu\text{m}$

(c)

Figure 12 cont'd. SEM micrographs of double Mg-Al₂TiO₅ coatings of different first and second coatings: (c) thickness of first and second coatings is 2 μm and 6 μm, respectively

Obtaining Pure CMZP Phase

Although over 40 CMZP coated samples have been calcined in air, none of them have yielded pure CMZP phase. The typical x-ray diffraction pattern is shown in Figure 13, indicating a strong peak of CaSiO₃ which originated from the oxidation of SiC and reaction of SiO₂ and CaO, creating CaSiO₃:

The results of these experiments pointed out that it is impossible to obtain pure CMZP phase when samples are fired in air. In order to obtain the pure phase, samples were fired in controlled atmospheres and the results are described below.

1. The samples were first fired in air at 400°C for 6 hours, then fired in a covered crucible fully filled with CMZP powder at 1200°C for 24 hours. Figure 14 shows the x-ray diffraction patterns showing the pure CMZP phase.

2. The samples were fired in a mildly reducing atmosphere. The samples were placed in a covered crucible with a small amount of carbon powder, and the lid was sealed with liquid K_2SiO_3 . It was important to use just a little carbon powder to keep the atmosphere mildly reducing. The x-ray diffraction pattern in Figure 15 shows the CMZP phase is nearly pure.
3. The samples were fired in a CO_2 atmosphere. The samples were placed in a covered crucible which was then filled with $CaCO_3$. At high temperatures $CaCO_3$ decomposes into CO_2 , keeping the atmosphere CO_2 -rich. The x-ray diffraction pattern in Figure 16 shows that the CMZP phase is nearly pure.
4. The samples were fired in a covered crucible sealed with liquid K_2SiO_3 . This results in an atmosphere in which the oxygen is less than in air but richer than in previous cases. The x-ray diffraction in Figure 17 shows only a partial CMZP phase formed.
5. The samples were fired in N_2 . The samples were fired in the tube furnace with a flow of N_2 . Carbon powder was found on the internal wall of the tube and on the surface of the samples, because SiC and N_2 reacted under high temperature, creating carbon:

This result pointed out that it is impossible to prevent oxidation when firing coated SiC samples in N_2 atmosphere. Table 6 shows the comparison of different coatings under different firing atmospheres.

Table 6. Comparison of different CMZP coatings under different firing atmospheres

Atmosphere	Method	Abundance of O_2	Purity of CMZP Phase
isolated from air	crucible with lid and fully filled with CMZP powder	no O_2	high
poor O_2	crucible with C and lid sealed with K_2SiO_3	poor	good
rich CO_2	crucible with lid and $CaCO_3$	poor	good
partial O_2	crucible with lid sealed with K_2SiO_3	partial	poor
air	in air	rich	poor

Figure 13. X-ray diffraction patterns of CMZP coating fired in air (a) and CMZP powder (b).

Figure 14. X-ray diffraction patterns of CMZP coating fired and isolated from air (a) and CMZP powder (b)

Figure 15. X-ray diffraction patterns of CMZP coating fired in an atmosphere of poor oxygen (a) and CMZP powder (b)

Figure 16. X-ray diffraction patterns of CMZP coating fired in an atmosphere of rich CO_2 (a) and CMZP powder (b)

Figure 17. X-ray diffraction patterns of CMZP coating fired in an atmosphere of partial oxygen (a) and CMZP powder (b)

Improving Mg-Al₂TiO₅ Coating Procedure

A procedure for coating Mg-Al₂TiO₅ to SiC utilizing a hydrolyzed solution of Mg-Al₂TiO₅ was described by Kang.⁹ However, the hydrolyzed solution is very sticky even though the concentration is small. It is, therefore, difficult to obtain homogeneous coating layers. Over 40 samples coated with Mg-Al₂TiO₅ utilizing hydrolyzed Mg-Al₂TiO₅ solution were tested; however, none of them had pure phase. The typical x-ray diffraction pattern is shown in Figure 18.

Figure 18. X-ray diffraction patterns of Mg-Al₂TiO₅ coating utilizing hydrolyzed solution (a) and Mg-Al₂TiO₅ powder (b)

The process has been changed as follows:

1. Coat the samples utilizing unhydrolyzed $\text{Mg-Al}_2\text{TiO}_5$ solution instead of hydrolyzed solution to decrease the viscosity and increase the concentration.
2. Place the samples in a container with saturated humidity for three days for hydrolysis.
3. Dry the samples in air at room temperature for three days.
4. Further dry the samples at 65°C for 12 hours.
5. Fire the samples in air at 400°C for 6 hours.
6. Coat the samples a second time, then hydrolyze and dry the samples similar to the first coating.

Figure 19 shows the x-ray diffraction patterns of the improved coatings and the formation of nearly pure $\text{Mg-Al}_2\text{TiO}_5$ phase.

Thermal Shock Resistance

CMZP Coatings

Thermal shock resistance of CMZP coatings was examined. The experimental results are shown in Table 7. Surface microstructure of coatings and adhesion between the coatings and substrates were examined by SEM. Figure 20 shows that the surface microstructure of the samples, after a thermal shock of 1000°C , exhibited cracks and small spalling. Figure 21 shows that after a 750°C thermal shock, cracks appeared but no spalling; and Figure 22 shows that after a 500°C thermal shock, no cracks were present.

Table 7. Thermal shock resistance of CMZP coated SiC samples

Sample	Heated Temperature and Results			
	300°C	500°C	750°C	1000°C
Group 1 (4 samples)	no cracks			
Group 2 (4 samples)		no cracks		
Group 3 (4 samples)			cracks	
Group 4 (4 samples)				cracks and small spalling

Figure 19. X-ray diffraction patterns of $\text{Mg-Al}_2\text{TiO}_5$ coating utilizing unhydrolyzed solution (a) and $\text{Mg-Al}_2\text{TiO}_5$ powder (b)

Figure 20. Surface microstructure of CMZP coated samples exhibited cracks and small spalling after a thermal shock of 1000°C

Figure 21. Surface microstructure of CMZP coated samples exhibited cracks after a thermal shock of 750°C

Figure 22. Surface microstructure of CMZP coated samples exhibited no cracks after a thermal shock of 500°C

Mg-Al₂TiO₅ Coating Samples

The thermal shock resistance of Mg-Al₂TiO₅ coated SiC samples was also examined. The experimental results are shown in Table 8. Surface microstructure of coatings and adhesion between the coatings and substrates were examined by SEM. Figure 23 shows the surface microstructure of the samples after a thermal shock of 1000°C exhibited cracks and small spalling. Figure 24 shows that after a 750°C thermal shock, cracks appeared; and Figure 25 shows that after a 500°C thermal shock, no cracks were present.

Table 8. Thermal shock resistance of Mg-Al₂TiO₅ coated SiC samples

Sample	Heated Temperature and Results			
	300°C	500°C	750°C	1000°C
Group 1 (4 samples)	no cracks			
Group 2 (4 samples)		no cracks		
Group 3 (4 samples)			cracks	
Group 4 (4 samples)				cracks and small spalling

Figure 23. Surface microstructure of Mg-Al₂TiO₅ coated samples exhibited cracks and small spalling after a thermal shock of 1000°C

Figure 24. Surface microstructure of Mg-Al₂TiO₅ coated samples exhibited cracks after a thermal shock of 750°C

Figure 25. Surface microstructure of Mg-Al₂TiO₅ coated samples exhibited no cracks after a thermal shock of 500°C

Alkali Corrosion Resistance

CMZP Coatings

Table 9 shows the weight loss and Table 10 shows the room temperature flexural strength of both as-received and corroded SiC samples determined by 4-point bending using an ATS Test System. To decrease the effect of random errors, the average strengths of every group were reported. Many other groups of CMZP coated and as-received samples were also examined and the statistical results were similar to the results as described above.

Table 9. Weight loss of CMZP coated and uncoated samples after sodium corrosion (%)

	1100°C		1000°C		900°C	
	Coated	Uncoated	Coated	Uncoated	Coated	Uncoated
Obtained Value	2.8	3.7	2.1	3.6	2.3	3.7
	2.4	3.6	2.0	3.5	2.7	3.4
	2.1	3.3	2.7	3.2	1.9	3.3
	2.2	2.6	2.6	2.5	2.1	2.4
Average Value	2.4	3.3	2.4	3.2	2.3	3.2

Table 10. Flexural strength of CMZP coated and uncoated SiC samples before and after sodium corrosion (MPa)

	Before Corrosion		1100°C		1000°C		900°C	
	Coated	Uncoated	Coated	Uncoated	Coated	Uncoated	Coated	Uncoated
Obtained Value	468	424	417	432	432	414	449	426
	455	468	469	407	411	432	438	397
	432	465	438	402	448	412	436	411
	444	447	425	410	436	398	443	408
Average Value	450	450	437	413	432	414	442	411

The sodium corrosion resistance of CMZP coated SiC samples was improved over that of uncoated samples as indicated in Figures 26 and 27. Compared to CMZP coated samples, uncoated samples exhibited a greater weight loss and reduction in strength. The SEM micrograph of uncoated SiC after corrosion, Figure 28, shows the formation of holes on the surface and considerable penetration of alkali.

SiC is thermodynamically unstable in air and relies on a thin film of SiO₂ for oxidation protection. The SiO₂ film on SiC, although very thin, is normally protective in an oxidizing atmosphere at high temperature. The presence of sodium with SiC dissolves the SiO₂ protective film and enhances oxidation. It is believed that the following reactions occur:

The protective SiO₂ film is dissolved to form Na₂SiO₃. Accelerated scale growth occurs because the silicate is liquid at 1000°C. The CMZP reacts with SiO₂ film on the surface of the SiC substrates and sodium to produce a more refractory layer, which assists in maintaining a continuous reaction layer and minimizes corrosion. The SEM micrograph in Figure 29 shows that a dense protective layer on the surface of CMZP coated SiC samples was formed after sodium corrosion. Figure 30 shows the distribution of Ca, Mg, Zr, P, and Si on the sample surface, obtained by EDX, which proves that the protective layer came from CMZP.

Figure 26. Weight loss of CMZP coated and uncoated SiC samples after sodium corrosion

Figure 27. Flexural strength of CMZP coated and uncoated SiC samples before and after sodium corrosion

Figure 28. Corrosion of uncoated SiC samples by sodium carbonate

Figure 29. Dense protective layer on surface of CMZP coated SiC samples formed after sodium corrosion

Figure 30. Distribution of Ca, Mg, Zr, P, and Si on sample surfaces, obtained by EDX, proves that the protective layer came from CMZP coating

Mg-Al₂TiO₅ Coatings

The sodium corrosion resistance of Mg-Al₂TiO₅ coated SiC samples was improved over that of uncoated samples as indicated in Tables 11 and 12 and Figures 31 and 32. Compared to Mg-Al₂TiO₅ coated SiC samples, uncoated samples exhibited a greater weight loss. Many other groups of Mg-Al₂TiO₅ coated and as-received samples were also examined and the statistical results were similar to the results as described above.

Table 11. Weight loss of Mg-Al₂TiO₅ coated and uncoated samples after sodium corrosion (%)

	1100°C		1000°C		900°C	
	Coated	Uncoated	Coated	Uncoated	Coated	Uncoated
Obtained Value	3.1	2.9	2.4	4.1	3.2	3.2
	2.8	3.0	2.2	3.8	2.1	3.7
	2.4	3.5	2.6	3.6	2.5	4.0
	2.3	3.8	3.3	3.0	2.3	4.3
Average Value	2.7	3.3	2.6	3.6	2.5	3.8

Table 12. Flexural strength of Mg-Al₂TiO₅ coated and uncoated SiC samples before and after sodium corrosion (Mpa)

	Before Corrosion		1100°C		1000°C		900°C	
	Coated	Uncoated	Coated	Uncoated	Coated	Uncoated	Coated	Uncoated
Obtained Value	464	469	424	401	441	434	447	419
	432	423	462	404	419	409	436	437
	453	446	441	413	456	404	432	416
	447	463	414	431	442	413	443	403
Average Value	449	450	435	412	439	415	440	419

Figure 31. Weight loss of Mg-Al₂TiO₅ coated and uncoated SiC samples after sodium corrosion

Figure 32. Flexural strength of Mg-Al₂TiO₅ coated and uncoated SiC samples before and after sodium corrosion

The mechanism of improving corrosion resistance of $\text{Mg-Al}_2\text{TiO}_5$ coated SiC samples is similar to that of CMZP coated samples described above. SEM micrograph, Figure 33, shows that a dense protective layer was formed on the surface of $\text{Mg-Al}_2\text{TiO}_5$ coated SiC samples after sodium corrosion. Figure 34 shows the distribution of Mg, Al, Ti, and Si on the sample surface, obtained by EDX, proving that the protective layer came from $\text{Mg-Al}_2\text{TiO}_5$ coating.

Figure 33. Dense protective layer on surface of $\text{Mg-Al}_2\text{TiO}_5$ coated SiC samples formed after sodium corrosion

Figure 34. Distribution of Al, Ti, and Si on sample surface, obtained by EDX, proves that the protective layer came from $\text{Mg-Al}_2\text{TiO}_5$ coating

100-Hour Slagging Combustion Test

CMZP Coated Samples

Figure 35 shows the SEM micrographs of the uncorroded and corroded areas of the CMZP coated samples. Figure 36 shows the XRD results of the uncorroded areas of the CMZP coated samples. The CMZP phase can be distinguished, although there were some other phases resulting from the slag. Figure 37 shows the EDX results of the uncorroded areas of the CMZP coated samples indicating the existence of elements Ca, Mg, Zr, and P. This proves the existence of the CMZP coating after the test in the coal combustion atmosphere at high temperatures. It can be seen that the uncorroded SiC was coated while the corroded SiC did not have the coating on it. It is clear that the CMZP coatings improve the corrosion resistance under a coal combustion atmosphere at high temperatures. It was noticed that the SiC substrate was corroded if there were defects in the CMZP coating; that is, the corroded areas originated from cracks or poor adhesion of the CMZP coating. So homogeneous and crack-free coatings as well as enhanced adhesion of the coating are important for quality coatings. There were also some corroded areas on the sample surface in which it was difficult to distinguish the CMZP phase because of interference from the slag. Figure 38 shows the result of EDX analysis, indicating that the peaks of Ca, Ma, Zr, and P were weak.

Mg-Al₂TiO₅ Coated Samples

The SEM results presented in Figure 39 show the uncorroded areas and corroded areas of the Mg-Al₂TiO₅ coated samples. The XRD result presented in Figure 40 shows the uncorroded areas of the Mg-Al₂TiO₅ coated samples, indicating the existence of Mg-Al₂TiO₅ phase, although there were some other phases from the slag. The EDX result presented in Figure 41 shows the existence of elements Al, Ti, and Mg, indicating the existence of Mg-Al₂TiO₅ coating after testing in the coal combustion atmosphere at high temperatures. It can be seen that, similar to CMZP coatings, the uncorroded SiC substrate had the Mg-Al₂TiO₅ coating while the corroded SiC substrate did not have the coating. Also the SiC substrate was corroded if there were defects in the Mg-Al₂TiO₅ coating; that is, the corroded areas originated from cracks or poor adhesion of the coating. Homogeneous and crack-free coatings as well as enhanced adhesion of the coatings are clearly important for high quality coatings. At the corroded areas the Mg-Al₂TiO₅ phase cannot be distinguished from the covering slag. The EDX result presented in Figure 42 shows the existence of the elements Al, Ti, and Mg; however, the peaks were weak.

(a)

(b)

Figure 35. SEM micrographs of uncorroded areas (a) and corroded areas (b) of the CMZP coated samples

Figure 36. X-ray diffraction of the uncorroded areas of the CMZP coating
 (a) and the sample before the corrosion test (b)

Spectrum: CM02
Comments:

Name: CM02

Figure 37. EDX spectrum on a cross-section of the uncorroded areas of the CMZP coating

Spectrum: CMZP3
Comments:

Name: CMZP3

Figure 38. EDX spectrum on a cross-section of the corroded areas of the CMZP coating

(a)

(b)

Figure 39. SEM micrographs of uncorroded areas (a) and corroded areas (b) of the $\text{Mg-Al}_2\text{TiO}_5$ coated samples

Figure 40. X-ray diffraction of the uncorroded areas of the Mg-Al₂TiO₅ coating (a) and the sample before the corrosion test (b)

Spectrum: MGALT13
Comments:

Name: MGALT13

Figure 41. EDX spectrum on a cross-section of the uncorroded areas of the $\text{Mg-Al}_2\text{TiO}_5$ coating

Spectrum: MGALT1
Comments:

Name: MGALT1

Figure 42. EDX spectrum on a cross-section of the corroded areas of the $\text{Mg-Al}_2\text{TiO}_5$ coating

Aging Process

Thermal Shock Resistance Test

a. CMZP Coated SiC Samples. The thermal shock resistance of aged and unaged CMZP coated SiC samples was determined. The samples were heated to 300, 500, 750, and 1000°C, respectively, then quenched in water at room temperature (25°C). The results are shown in Table 13. The surface microstructure of coatings and adhesion between the coatings and substrates were examined by SEM. The surface microstructure of the aged and unaged samples after a thermal shock of 1000°C and 750°C (Figures 43, 44, 45, and 46) shows that the aging process improved the quality of CMZP coatings.

Table 13. The thermal shock resistance of aged and unaged CMZP coated SiC samples

Sample	Heated Temperature and Results			
	300°C	500°C	750°C	1000°C
Aged (4 samples)	No cracks	No cracks	Small cracks	Cracks
Unaged (4 samples)	No cracks	Small cracks	Cracks	Cracks and small spalling

Figure 43. Surface microstructure of aged CMZP coated samples after a thermal shock of 1000°C

Figure 44. Surface microstructure of unaged CMZP coated samples after a thermal shock of 1000°C

Figure 45. Surface microstructure of aged CMZP coated samples after a thermal shock of 750°C

Figure 46. Surface microstructure of unaged CMZP coated samples after a thermal shock of 750°C

b. Mg-Al₂TiO₅ Coated SiC Samples. The thermal shock resistance of aged and unaged Mg-Al₂TiO₅ coated SiC samples was tested. The samples were heated to 300, 500, 750, and 1000°C, respectively, then quenched in water at room temperature (25°C). The results are shown in Table 14. The surface microstructure of coatings and adhesion between the coatings and substrates were examined by SEM. The surface microstructure of the aged and unaged samples after a thermal shock of 1000°C and 750°C (Figures 47, 48, 49, and 50) shows that the aging process improved the quality of Mg-Al₂TiO₅ coatings.

Table 14. Thermal shock resistance of aged and unaged Mg-Al₂TiO₅ coated SiC samples

Sample	Heated Temperature and Results			
	300°C	500°C	750°C	1000°C
Aged (4 samples)	No cracks	No cracks	Small cracks	Cracks
Unaged (4 samples)	No cracks	Small cracks	Cracks	Cracks and small spalling

Figure 47. Surface microstructure of aged Mg-Al₂TiO₅ coated samples after a thermal shock of 1000°C

Figure 48. Surface microstructure of unaged Mg-Al₂TiO₅ coated samples after a thermal shock of 1000°C

Figure 49. Surface microstructure of aged Mg-Al₂TiO₅ coated samples after a thermal shock of 750°C

Figure 50. Surface microstructure of unaged Mg-Al₂TiO₅ coated samples after a thermal shock of 750°C

Alkali Corrosion Resistance Test

a. CMZP Coated SiC Samples. The alkali corrosion resistance of both aged and unaged CMZP coated SiC samples was examined by determining the weight loss and flexural strength degradation of samples exposed to a sodium-containing atmosphere. The room temperature flexural strength of both aged and unaged SiC samples was determined by 4-point bending using an ATS Test System. To decrease the random errors the average strengths of every group were selected. The distribution of Ca, Mg, Zr, P, and Si on sample surfaces both before and after corrosion were examined by EDX.

The sodium corrosion resistance of aged CMZP coated SiC samples improves over that of unaged samples as indicated in Tables 15 and 16 and Figures 51 and 52. Compared to aged CMZP coated SiC samples, unaged samples exhibited a greater weight loss and reduction in strength.

Table 15. Weight loss of aged and unaged CMZP coated SiC samples after sodium corrosion (%)

	1100°C		1000°C		900°C	
	Aged	Unaged	Aged	Unaged	Aged	Unaged
Obtained Value	2.5	2.8	2.2	2.1	2.2	2.3
	2.3	2.4	2.2	2.0	2.1	2.7
	2.1	2.1	2.4	2.7	2.1	1.9
	2.1	2.2	2.3	2.6	1.7	2.1
Average Value	2.3	2.4	2.3	2.4	2.0	2.3

Table 16. Flexural strength of aged and unaged CMZP coated SiC samples before and after sodium corrosion (MPa)

	Before Corrosion		1100°C		1000°C		900°C	
	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged
Obtained Value	442	468	429	417	448	432	449	449
	453	455	467	469	424	411	436	338
	455	432	457	438	427	448	453	436
	450	444	411	425	436	436	442	443
Average Value	450	450	441	437	434	432	445	442

Many other groups of aged and unaged samples were also examined and the statistical results were similar to the results described above.

Figures 53 and 54 and Table 17 show the distribution of Ca, Mg, Zr, P, and Si on the aged and unaged sample surfaces after sodium corrosion at 1000°C obtained by EDX. This proves that the aging process improves the quality of CMZP coatings.

Figure 51. Weight loss of aged and unaged CMZP coated SiC samples after sodium corrosion

Figure 52. Flexural strength of aged and unaged CMZP coated SiC samples before and after sodium corrosion.

Spectrum: CMZP-A-2
Comments:

Name: CMZP-A-2
Comments:

Centroid (KeV)	Gross Area	Normalized	Comments
1.260	3112.47	2.09	Mgk
1.743	115377.9	77.36	Sik
2.037	22125.63	14.83	Zrl
3.717	5922.33	3.97	Cak
6.447	2611.99	1.75	

Figure 53. Distribution of Ca, Mg, Zr, P, and Si on aged CMZP coated sample surfaces, obtained by EDX

Spectrum: CMZP-A-3
Comments:

Name: CMZP-A-3
Comments:

Centroid (KeV)	Net Area	Normalized	Comments
1.743	75669.01	85.43	Sik
2.058	9944.37	11.23	Zrl
3.717	1885.15	2.13	Cak
4.032	500.36	0.56	
15.834	577.84	0.65	

Figure 54. Distribution of Ca, Mg, Zr, P, and Si on unaged CMZP coated sample surfaces, obtained by EDX

Table 17. Distribution of Ca, Mg, Zr, P, and Si on the sample surfaces after sodium corrosion at 1000°C (%)

Aged				Unaged			
Ca	Mg	Zr, P*	Si	Ca	Mg	Zr, P*	Si
3.97	2.09	14.83	77.36	2.13	0	11.23	85.43

*The peaks of Zr and P overlap

b. Mg-Al₂TiO₅ Coated SiC Samples. The alkali corrosion resistance of both aged and unaged Mg-Al₂TiO₅ coated SiC samples was examined by determining the weight loss and flexural strength degradation of samples exposed to sodium containing atmospheres.

The sodium corrosion resistance of aged Mg-Al₂TiO₅ coated SiC samples is improved over that of unaged samples as indicated in Tables 18 and 19 and Figures 55 and 56.

Table 18. The weight loss of aged and unaged Mg-Al₂TiO₅ coated SiC samples after sodium corrosion (%)

	1100°C		1000°C		900°C	
	Aged	Unaged	Aged	Unaged	Aged	Unaged
Obtained Value	2.1	3.1	2.7	2.4	2.5	3.2
	2.1	2.8	2.4	2.2	2.0	2.1
	2.6	2.4	2.5	2.6	2.2	2.5
	2.4	2.3	2.3	3.3	2.4	2.3
Average Value	2.3	2.7	2.5	2.6	2.3	2.5

Table 19. Flexural strength of aged and unaged Mg-Al₂TiO₅ coated SiC samples before and after sodium corrosion (MPa)

	Before Corrosion		1100°C		1000°C		900°C	
	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged
Obtained Value	432	464	423	424	438	441	435	447
	458	432	450	462	431	419	451	436
	455	453	451	441	453	455	441	432
	452	447	426	414	452	442	449	443
Average Value	449	449	438	435	444	439	444	440

Compared with aged Mg-Al₂TiO₅ coated samples, unaged samples exhibited a greater weight loss and reduction in strength. Many other groups of aged and unaged samples were also examined and the statistical results were similar to the results described above.

Figure 55. Weight loss of aged and unaged Mg-Al₂TiO₅ coated SiC samples after sodium corrosion

Figure 56. Flexural strength of aged and unaged Mg-Al₂TiO₅ coated SiC samples before and after sodium corrosion

Figures 57 and 58 and Table 20 show the distribution of Mg, Al, Ti, and Si on the aged and unaged sample surfaces after sodium corrosion at 1000°C obtained by EDX, which proves that the aging process improves the quality of Mg-Al₂TiO₅ coatings.

Table 20. Distribution of Mg, Al, Ti, and Si on the sample surfaces after the sodium corrosion at 1000°C (%)

Aged				Unaged			
Mg	Al	Ti	Si	Mg	Al	Ti	Si
0.23	5.00	9.36	81.89	0.12	2.69	3.29	92.27

Figure 57. Distribution of Mg, Al, Ti, and Si on aged Mg-Al₂TiO₅ coated sample surfaces, obtained by EDX

Figure 58. Distribution of Mg, Al, Ti, and Si on unaged Mg-Al₂TiO₅ coated sample surfaces, obtained by EDX

Conclusions

1. CMZP and Mg-Al₂TiO₅ coatings on dense SiC substrates using sol-gel techniques were developed.
2. The thickness and quality of both CMZP and Mg-Al₂TiO₅ coatings were found to depend on the solution concentration and lift rate.
3. Double coatings were applied to obtain homogeneous and crack-free coatings. The quality of double coatings was influenced by the different thickness of the first and second coatings.
4. The CMZP coated samples were fired in controlled atmospheres to obtain the pure CMZP phase.
5. Unhydrolyzed Mg-Al₂TiO₅ solution was utilized instead of the hydrolyzed solution to improve the quality of Mg-Al₂TiO₅ coatings.

6. An aging process was found to improve the quality of CMZP and $\text{Mg-Al}_2\text{TiO}_5$ coatings.
7. CMZP and $\text{Mg-Al}_2\text{TiO}_5$ coatings exhibit good thermal shock resistance.
8. CMZP and $\text{Mg-Al}_2\text{TiO}_5$ coatings improve alkali corrosion resistance of SiC.

Part 2 Evaluation of Cause and Severity of Ceramic Heat Exchanger Deterioration and Failure Under Coal Combustion Conditions

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 stability.⁵⁸ Unfortunately, when subjected to coal combustion atmospheres containing alkali species, Si_3N_4 undergoes severe oxidation and eventually loses its properties.^{59,60} Because oxides usually exhibit a better resistance to alkali corrosion than non-oxide materials,^{61,62} 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 Al_2TiO_5) and calcium magnesium zirconium phosphate (CMZP), with formula $(\text{Ca}_{0.6}, \text{Mg}_{0.4})\text{Zr}_4(\text{PO}_4)_6$, were selected as coatings because of their compatibility with Si_3N_4 . Mg- Al_2TiO_5 is a well known oxide possessing 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 Al_2TiO_5 , it yields outstanding thermal properties and possibly good resistance to alkali corrosion. Previous work conducted at Virginia Tech has demonstrated the possibility of depositing Al_2TiO_5 and CMZP coatings on SiC and Si_3N_4 using sol-gel and dip-coating techniques, and exposures to alkali-containing atmospheres have indicated improved alkali corrosion resistance.^{63,64,65}

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.

Literature Review

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 temperatures and that they rely on a thin film of SiO_2 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.⁶⁶⁻⁷¹ They indicated that a 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 SiO_2 layer. Normally, the silica layer can protect Si_3N_4 up to 1200°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 further oxidize the ceramic.⁷²

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.^{73,74} The samples were airbrushed with a saturated solution of Na_2CO_3 or Na_2SO_4 , 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 Na_2CO_3 or Na_2SO_4 to form a sodium silicate melt by reaction with SiO_2 , 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°C and 925 to 1150°C , respectively.^{60,75} 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-thirds of the initial value.

To simulate aircraft turbine environments, Fox and Smialek devised the burner rig tests.⁷⁶ The method consisted of subjecting the samples to a combustion flame seeded with 2 ppm Na impurities, which led to the deposition of an 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.,⁷⁷ who investigated the corrosion of silicon-based ceramics in an NaNO_3 atmosphere. 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 .

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,⁷⁸ the field of sol-gel is currently receiving much attention. Over the last thirty-five years, this area of science has been extensively studied and its practice is now relatively well known.⁷⁹ 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 inside of tubes. However, these advantages must be balanced against the high cost of raw materials, the long processing time involved, the non-uniformity of the films, and the formation of cracks upon drying.⁸⁰

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 semi-

solid phase known as gel. Commonly, the most preferred starting reagents are metal alkoxides, with the general formula:

where M = metal

R = alkyl group such as methyl (CH_3), ethyl (C_2H_5), propyl (C_3H_7)
or butyl (C_4H_9)

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 into the sol. In this process, the alkoxide groups (OR) are replaced stepwise by hydroxyl groups (OH) as summarized below.

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.^{79,80} 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).

The hydrolysis of the metal alkoxide particles is usually catalyzed by the addition of an acid or base.⁸¹ In acidic solution, the hydrolysis reaction proceeds by electrophilic attack.^{82,83} As illustrated in Figure 59 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.^{79,82} 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 60.

Figure 59. Acid catalyzed hydrolysis by electrophilic reaction mechanism

Figure 60. Base-catalyzed hydrolysis by nucleophilic reaction mechanism

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

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.⁸¹ Its structure is strongly dependent on the water content in the system and whether an acid or base was used as the 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 base-catalyzed solutions, branched clusters are preferentially formed and their propensity to coalesce is responsible for the gelation of the solution.⁸²

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.⁸⁴ 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 μm .

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 exists 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 areas of interest are best summarized in the sol-gel tree of Dislich (see Figure 61).⁸⁵

Figure 61. Sol-gel tree

In this section emphasis will be placed on three promising commercial niches where the sol-gel process has proven 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 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.^{85,86} 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 advantages of the sol-gel process) is considered. The fine spherical shapes (e.g. 1 μm), 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 of 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.^{80,87}

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) makes large quantity production commercially nonviable. 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.⁸⁸ The second reason sol-gel science is appealing to the glass industry lies in its potential for innovativeness. Indeed, a wide range of new products with desirable properties cannot 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.⁸⁵ Wide perspectives for the synthesis of glasses with novel compositions 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: dip-coating, spin-coating, and spray-coating.⁸⁰ In the following paragraph, only the first technique is presented for it is 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^{88,89} and the acquisition of relatively low cost non-sophisticated equipment.^{80,90} 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.^{87,91} 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 gravity and surface tension must also be considered.⁹² For multicomponent systems, it was reported that the rate of hydrolysis varied from one 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 about this subject.⁹⁰

Mg-doped Al_2TiO_5 and CMZP ceramic oxides

Mg-doped Al_2TiO_5

Aluminum titanate, Al_2TiO_5 , is a synthetic oxide ceramic well known for its high melting point, low thermal conductivity, near zero thermal expansion coefficient ($\alpha_a = +9.8 \cdot 10^{-6}/^{\circ}C$, $\alpha_b = +20.6 \cdot 10^{-6}/^{\circ}C$, $\alpha_c = -1.4 \cdot 10^{-6}/^{\circ}C$, $\alpha_l = 2 \cdot 10^{-6}/^{\circ}C$), and excellent thermal shock resistance.^{93,94} Regarding its properties, Al_2TiO_5 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 engine swirl chambers.⁹⁵ 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 grains 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- Al_2TiO_5 or Al_2TiO_5 - ZrTiO_4 - ZrO_2 systems, in order to strengthen the ceramic,^{96,97} or synthesized submicronic powders by sol-gel to sinter pore-free compact oxides.⁹⁸

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 β - Al_2TiO_5 phases, were yielded by the addition of small oxide amounts such as MgO or Fe_2O_3 .^{99,100}

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.⁶³ These results were confirmed by M. Kang and S. Yang, who successfully developed Mg-doped Al_2TiO_5 coatings on SiC to increase its oxidation resistance.^{64,65}

CMZP

Similar to Al_2TiO_5 , 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 $\text{NaZr}_2(\text{PO}_4)_3$ (NZP) family first reported in the literature by L. O. Hagman and P. K. Kierkegaard in 1968.¹⁰¹ NZP family-based materials owe their properties to an outstanding crystal structure composed of strongly bonded, corner-sharing ZrO_6 octahedra and PO_4 tetrahedra in an open three-dimensional framework, which allows a variety of ionic substitutions.¹⁰²⁻¹⁰⁴ This particular feature has been exploited by many researchers to develop innovative materials such as $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (NASICON) for fast ionic conductors or new solid electrolytes where phosphor in the NZP was replaced by silicon sodium pairs.^{105,108}

More recently, a great amount of research conducted at Virginia Tech has been aimed toward 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 $(\text{Ca}_{1-x}\text{Mg}_x)\text{Zr}_4(\text{PO}_4)_6$, the research group of Dr. J. J. Brown has been able to create a near zero thermal expansion material, with formula $(\text{Ca}_{0.6}\text{Mg}_{0.4})\text{Zr}_4(\text{PO}_4)_6$.^{109,110} The ceramic contracts along the a axis and expands along the c axis, yielding a bulk coefficient of thermal expansion of $0.1 \times 10^{-6}/^\circ\text{C}$. The corrosion resistance of silicon-based ceramic coated with CMZP was investigated by T. K. Li, M. Kang, and S. Yang, and the three authors clearly witnessed reduced corrosion.^{64,65,111,112}

Experimental Procedure

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, 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, 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, then immersed in a 1:1 HNO_3 solution for 6 hours. Then they were washed with deionized water and dried at 110°C for 2 hours. Next, the 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.

Preparation of sol-gel solutions

CMZP sol-gel

The precursors selected for the sol-gel are calcium chloride (CaCl_2), magnesium perchlorate hexahydrate ($\text{Mg}(\text{ClO}_4) \cdot 6\text{H}_2\text{O}$), zirconium propoxide ($\text{Zr}(\text{C}_3\text{H}_7\text{O})_4$), and triethyl phosphate ($(\text{C}_2\text{H}_5\text{O})_3\text{P}(\text{O})$). The stoichiometric weight amounts calculated for the precursors are $\text{Ca} : \text{Mg} : \text{Zr} : \text{P} = 1 : 1.393 : 28.110 : 16.413$. First, CaCl_2 and $\text{Mg}(\text{ClO}_4) \cdot 6\text{H}_2\text{O}$ were mixed in ethyl alcohol and HCl was added drop by drop until a pH between 2.2 and 4.0 was reached. Then, $\text{Zr}(\text{C}_3\text{H}_7\text{O})_4$ and $(\text{C}_2\text{H}_5\text{O})_3\text{P}(\text{O})$ 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.

Mg-Doped Al_2TiO_5 sol-gel

The alkoxides selected for the sol-gel solution are magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), aluminum tri-sec butoxide ($\text{Al}[\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{O}]_3$), and titanium butoxide ($\text{Ti}[\text{CH}_3(\text{CH}_2)_3\text{O}]_4$). The stoichiometric weight amounts calculated for the precursors are $\text{Al} : \text{Ti} : \text{Mg} = 1 : 0.852 : 0.056$. First, the three precursors were mixed and then a solution of ethyl alcohol and nitric acid and 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 $\text{Mg}_{0.1}\text{Al}_{1.8}\text{Ti}_{1.1}\text{O}_5$ sol between 4.0 and 6.5 cp. The solution obtained was clear with a slight yellow color.

Coating Techniques

Mg-doped Al_2TiO_5 coating

To obtain Mg-doped Al_2TiO_5 coatings, Si_3N_4 samples were immersed in the sol-gel 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% relative humidity at room temperature for 72 hours. The gel was then condensed in air at room temperature for an additional 48 hours and at 65°C for 24 hours. Removal of all solvents and crystallization was 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, 300, and 400°C at a heating rate of $1^\circ\text{C}/\text{min}$ and remained at each step for 1.5 hours. Then, to prevent the crystallization of Al_2O_3 and TiO_2 , they were rapidly heated to 1300°C at a rate of $10^\circ\text{C}/\text{min}$. After crystallization, the specimens were cooled to room temperature at a rate of $5^\circ\text{C}/\text{min}$. Figure 62 shows the heat treatment schedule for Mg-doped Al_2TiO_5 coatings.

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 and 40-80% relative humidity for 72 hours. Condensation was achieved by drying the samples at room temperature 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, 300, 400, and 500°C at a heating rate of 0.5°C/min and remained at each step for 2 hours. Next, they were heated at a 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 63 shows the CMZP coating process and heat treatment schedule in more detail.

Thermal Shock Resistance Test

The thermal shock resistance of coated and uncoated specimens with dimensions of 5 x 5 x 3 mm was investigated. Five groups of three samples were heated to 600, 700, 800, 900, and 1000°C, respectively, 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).

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 Si_3N_4 MOR (modulus of rupture) bars coated with CMZP and Mg-doped Al_2TiO_5 , respectively, were first heated to 200°C and dip-coated in an NaNO_3 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.% NaNO_3 concentration at 1000°C for 48 h. A scheme of the apparatus used for the alkali corrosion experiment is given in Figure 64. Although Na_2SO_4 is the most common melt encountered in industrial systems, NaNO_3 (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 NaCO_3 or Na_2SO_4 .⁷⁷ As illustrated in Figure 64, the apparatus consists of two separate heating zones. On the gas inlet side an alumina boat filled with NaNO_3 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 to entering the alumina tube, the compressed air was filtered to remove moisture and CO_2 . This was achieved by using a four-compartment plastic tube filled with silica gel, drierite, activated alumina, and silica gel, respectively.

Add solution of ethyl alcohol and nitric acid

Add deionized water and adjust pH and viscosity

Dip-coating

RT, 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

↓ *5°C/min*

RT

Figure 62. Heat treatment schedule for Mg-doped Al_2TiO_5 coatings

Figure 63. Heat treatment schedule for CMZP coatings

To investigate the strength degradation as a function of time, a 1000°C and 360-hour corrosion experiment was conducted. MOR bars of Si_3N_4 measuring 3 x 4 x 24 mm were heated to 200°C, dip-coated in an NaNO_3 saturated aqueous solution, then placed in a furnace containing a crucible filled with sodium nitrate. By measuring the weight loss of NaNO_3 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 65.

Figure 64. Schematic of the alkali corrosion apparatus used with four-point bending test

Figure 65. Schematic of the alkali corrosion apparatus used for the aging test

Corrosion Resistance Evaluation

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.

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, 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.

Results and Discussion

Surface Pre-Treatment

Contact angle tests were conducted to assess the effectiveness of the surface preparation. Five measurements were performed on each sample 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 21. 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 preparations as indicated by the small contact angle ($< 5^\circ$).

Table 21. Contact angle for as-received Si_3N_4 and Si_3N_4 surface treated for CMZP and Mg-doped Al_2TiO_5

	Si_3N_4 as received	Si_3N_4 surface treated for CMZP	Si_3N_4 surface treated for Mg-doped Al_2TiO_5
Contact angle ($^\circ$)	70.7	< 5	< 5

After calcination at 1200°C for 6 hours, the formation of a 1 μm thick silica layer was observed. Figure 66 shows a cross-section and corresponding EDX (Model ISI SX-40, beryllium window) elemental mappings for Si_3N_4 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 66. SEM photomicrograph of a fractured surface for a surface-treated Si_3N_4 and corresponding elemental mappings

Sol-gel coatings characterization

Sol-gel derived powders

In the early stage of this research, it was necessary to confirm whether the sol-gel procedure devised successfully 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 Al_2TiO_5 sol-gels are presented in Figure 67. Using x-ray data given for $(\text{ZrO})_2\text{P}_2\text{O}_7$ (ZP), $\text{CaZr}_4(\text{PO}_4)_6$ (CZP), $\text{MgZr}_4(\text{PO}_4)_6$ (MZP), $(\text{Ca}_{0.6}\text{Mg}_{0.4})\text{Zr}_4(\text{PO}_4)_6$ (CMZP), TiO_2 , Al_2O_3 and Mg-doped Al_2TiO_5 powders,^{99,100,113,114} 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 in previous research.⁶³⁻⁶⁵ No peaks of TiO_2 and Al_2O_3 were evidenced, suggesting that the addition of Mg^{2+} succeeded in stabilizing the compound.

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

CMZP coating

Homogeneous and crack-free CMZP coatings were successfully deposited using the sol-gel and dip-coating techniques. Figure 68 presents a micrograph 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

Figure 67. XRD patterns of a) CMZP calcined powder, b) Mg-doped Al_2TiO_5 calcined powder

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 Si_3N_4 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 69. 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, SiO_2 , and the sintering additives, Al_2O_3 and Y_2O_3 , 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 68. SEM micrograph of CMZP coating

Figure 69. SEM micrograph of a fractured surface for Si₃N₄ coated with CMZP and corresponding elemental mappings

Mg-doped Al_2TiO_5 coating

For Mg- Al_2TiO_5 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 Al_2TiO_5 sol-gel did not give the expected coating as shown in Figure 70. The SEM micrograph features an aluminum titanium silicate glassy phase with the presence of needle-like particles at the surface. EDX analyses indicate that these particles have a 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.¹¹⁵ 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 70. SEM micrograph of Mg-doped Al_2TiO_5 coating

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 Al_2TiO_5 coatings should yield an excellent thermal shock resistance since their respective coefficient of thermal expansion ($0.1\text{-}2 \times 10^{-6}/^\circ\text{C}$ for CMZP and $2\text{-}3 \times 10^{-6}/^\circ\text{C}$ for Mg-doped Al_2TiO_5)

matches that for Si_3N_4 ($3 \times 10^{-6}/^\circ\text{C}$). The experimental results presented in Table 22 are consistent with the above analysis and the data provided by previous workers.^{64,65,111,112} 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 Si_3N_4 and the coatings as shown in Figure 71. 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 Si_3N_4 bulk as results with uncoated samples indicate.

Table 22. Thermal shock resistance of coated and uncoated Si_3N_4 samples

Temperature (°C)	500	600	700	800	900	1000
Si_3N_4	no cracks	no cracks	no cracks	cracks	cracks	Cracks
CMZP	no cracks	no cracks	no cracks	cracks	cracks	cracks
Mg-doped Al_2TiO_5	no cracks	no cracks	no cracks	cracks	cracks	cracks

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 imparts 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 continues with the repetition of steps 2 and 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.

(a)

(b)

Figure 71. Surface of microstructure of a) CMZP and b) Mg-doped Al₂TiO₅ after thermal shock test at 800°C

Corrosion of CMZP coated samples

Si_3N_4 samples coated three times with CMZP sol-gel were tested in an NaNO_3 atmosphere at 1000°C for 48 h using the apparatus shown in Figure 64. 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 72 shows the EDX spectra of the surface of CMZP coated Si_3N_4 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 NaNO_3 melt. As can be observed in Figure 72, 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 73 a). Using this information, an attempt was made to label the different peaks yielded by XRD. For the uncoated Si_3N_4 specimen the corrosion product layer primarily consists of sodium silicate phase, $\text{Na}_2\text{O} \cdot x\text{SiO}_2$, while for specimens coated with CMZP, XRD patterns evidenced the presence of other silicate phases along with sodium silicate. Table 23 summarizes the different particles observed for CMZP-coated Si_3N_4 and their possible identification.

Table 23. Possible phases present in the corrosion product layer

Particle or area	Element detected with EDX	Possible phase identification
needle like particle	Al, Si, O, Na	NaAlSiO_4 (sodium aluminum silicate)
nodular particle	Y, Si	Y_2SiO_5 (yttrium silicate)
coarse area	Si, Na, O	$\text{Na}_2\text{O} \cdot x\text{SiO}_2$ (sodium silicate)
smooth region	Ca, Zr, P, Si, O	SiZr (zirconium silicate) $\text{CaZr(PO}_4)_2$ (calcium zirconium phosphate) $\text{CaZrSi}_2\text{O}_7$ (calcium zirconium silicate) Ca_2SiO_7 (calcium silicate)

Figure 72. EDX spectrum of CMZP coatings a) before corrosion b) after corrosion

Figure 73a. SEM micrograph of CMZP coating after corrosion

Figure 73b. EDX elemental mapping for CMZP coating after corrosion

To study the attacked microstructure of the ceramic, the corrosion products were first removed during a two-hour treatment in H_2O . 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 Si_3N_4 as received and Si_3N_4 coated with CMZP, respectively. The morphologies of the corrosion scale for uncoated and coated specimens are depicted in Figure 74. It can be seen that the two micrographs 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).^{65,77} Micrographs of the attacked morphology are presented in Figure 75. As expected, two different features were evidenced. For the uncoated Si_3N_4 specimen, β -silicon nitride grains were observed, suggesting an attack of the ceramic at the grain boundary as reported by many other investigators⁷³⁻⁷⁷ while no or very little attack at the grain boundary phase was evidenced with CMZP coating.

Corrosion of Mg-doped Al_2TiO_5 coated samples

SEM micrograph and corresponding elemental mappings obtained for Mg-doped Al_2TiO_5 corroded specimens are presented in Figure 77 and indicate that the needle-like particles are preferentially attacked by the NaNO_3 melt. The attacked morphology obtained after water leach and a mild HF treatment (see Figure 78) features some Si_3N_4 grains, which tends to suggest that the coating did not preserve the Si_3N_4 .

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 a 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 evidence at the surface of the glassy phase. Their number witnessed the extent of the oxidation attack and was significantly larger for Si_3N_4 as received and coated with Mg-doped Al_2TiO_5 .

(a)

(b)

Figure 74. SEM micrographs of the corrosion scale obtained after water leach for a) uncoated Si_3N_4 , and b) Si_3N_4 coated originally with CMZP

(a)

(b)

Figure 75. SEM micrographs 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

Figure 76. SEM micrograph 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 an NaNO_3 containing atmosphere

Figure 77. SEM micrograph 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 an NaNO_3 containing atmosphere

For Si_3N_4 as-received specimens, the associated x-ray maps shown in Figure 78 yielded an even distribution of Si, O, Al, and Na, indicating the formation of a sodium aluminum silicate phase containing a 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 to a lesser extent as indicated in Figure 79. For Mg-doped Al_2TiO_5 coatings, it was determined from Si, O, Al, and Na maps that the corrosion layer consisted primarily of a sodium aluminum silicate phase with a small quantity of Mg, Ti, and Y as featured in Figure 80. 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.

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 to the uniform surface recession mechanism. The mode of attack is therefore similar to the one encountered with as received Si_3N_4 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 softening agents by lowering the solidus temperature of the grain boundary phase.⁷⁷

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 on 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 81 and Table 24. 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 24 and calculated with a t test for a level of confidence of 95%, indicate that the strength reduction observed is significant. A comparison of the three sets of specimens with uncoated Si_3N_4 taken as reference (-14.4% of initial strength) shows 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, to a large extent, reduced the fractural strength of Si_3N_4 (-14.9% of initial strength).

Figure 78. Fractography and corresponding EDX mappings of as-received Si_3N_4 after 96-hour corrosion at 1000°C

Figure 79. Fractography and corresponding EDX mappings Si_3N_4 coated with CMZP after 96-hour corrosion at 1000°C

Figure 80. Fractography and corresponding EDX mappings of Si_3N_4 coated with Mg-doped Al_2TiO_5 after 96-hour corrosion at 1000°C

Figure 81. Four point bending fractural strength of coated and uncoated Si₃N₄ before and after 96-hour corrosion at 1000°C

Table 24. Alkali corrosion resistance of coatings

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

The three-point bend flexural strength and weight loss measurements as a function of time were also investigated and are shown in Figures 82 and 83, 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 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 83, 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 78. 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 ($\geq 10 \mu\text{m}$) and their content. Duckworth has proposed an experimental relationship between strength and porosity¹¹⁶ in which the strength decrease is directly correlated to the pore size and content as indicated in the following equation:

$$\sigma_p = \sigma_o e^{-BP}$$

where σ_p is the strength of the ceramic with porosities

σ_o is the strength of the ceramic without porosities

B is a constant which depends on the distribution and morphology of the pore

P is the fractional pore content.

Based on this equation, the higher fractural 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 82. Three-point bend flexural strength as a function of time after sodium vapor corrosion at 1000°C

Figure 83. Weight loss measurements as a function of time after sodium vapor corrosion at 1000°C

Conclusions

In this work, $(\text{Ca}_{0.6}\text{Mg}_{0.4})\text{Zr}_4(\text{PO}_4)_6$ (CMZP) and Mg-doped Al_2TiO_5 coatings were deposited on Si_3N_4 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 μm thick films composed of 2-3 μm 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 atmospheres containing sodium nitrate (NaNO_3) 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 Si_3N_4 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 their structural properties better 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.

References

1. D.A. Hirschfeld, S.M. VanAken, T.K. Li, Y.P. Yang, and J.J. Brown, *Proceedings of the Annual Automotive Technology Development Contractor's Coordination Meetings*, p. 239 (1990).
2. D. Hirschfeld, Y. Yang, T.K. Li, and J.J. Brown, *Proceedings of the Annual Automotive Technology Development Contractor's Coordination Meetings*, pp. 145-147 (1991).
3. D. Hirschfeld, D. Liu, and J.J. Brown, *Proceedings, 4th International Symposium on Ceramic Materials and Components for Engines*, Goteborg, Sweden (1991).
4. J.J. Brown and N.R. Brown, "Durability Testing of Ceramic Particulate Filters under PFBC Conditions," EPRI TR-103286, Project 3161-06, Final Report, Nov. 1993.
5. J.J. Brown, D.A. Hirschfeld, D.M. Liu, Y. Yang, T.K. Li, R.E. Swanson, S. VanAken, and J.M. Kim, "Ceramic Materials with Low Thermal Conductivity and Low Coefficients of Thermal Expansion," U.S. Patent 5,102,836, April 7, 1992.
6. T. Sun, N.R. Brown, and J.J. Brown, "Investigations of Long-Term Thermal/Chemical Degradation of Ceramic Filter Materials," Final Report, Center for Advanced Ceramic Materials, Virginia Tech, (1991).
7. T.K. Li, D.A. Hirschfeld, and J.J. Brown, "Thin Film Coatings of $(\text{Ca}_{0.6}\text{Mg}_{0.4}\text{Zr}_4\text{PO}_4)_6$ on Si_3N_4 and SiC ," *J. Mater. Res.*, **9** [8] 2014 (1994).
8. J.J. Brown, N.R. Brown, and T. Sun, "Sol-Gel Beta-Aluminum Titanate Thin Film Coating," U.S. Patent 5,407,479, April 18, 1995.
9. M. Kang, "Alkali/Steam Corrosion Resistance of Commercial SiC Products Coated with Sol-Gel Deposited Mg-Doped Al_2TiO_5 and CMZP," Master's Thesis, Dept. of Materials Science and Engineering, Virginia Tech (1994).
10. Y. Inomata, *Silicon Carbide Ceramics-1*, p. 9, ed. S. Somoya and Y. Inomata, Elsevier Science Publishing, New York (1991).
11. A. Bennett, "Requirements for Engineering Ceramics in Gas Turbine Engines," *Mater. Sci. Technol.*, **2**, 895-99 (1986).

12. D.W. Richerson, *Modern Ceramic Engineering*, pp. 116-34, Marcel Dekker, New York, New York (1982).
13. H. Kim, and A.J. Moorehead, "High-Temperature Gaseous Corrosion of Silicon Nitride in H₂-H₂O and Ar-O₂ Environments," *J. Am. Ceram. Soc.*, **73** [10], 3007-14, (1990).
14. E. Gulbransen, K. Andrew, and F. Brassart, "The Oxidation of SiC at 1150 to 1400°C and at 9×10^{-3} to 5×10^{-1} Torr Oxygen Pressure," *J. Electrochem. Soc.*, **113** [12] 1311-14, 1966.
15. W. Vaughn and H. Maahs, "Active to Passive Transition in the Oxidation of Silicon Carbide and Silicon Nitride in Air," *J. Am. Ceram. Soc.*, **73** [6] 1540-43 (1990).
16. S.M. McNallan and D. Park, "Active Oxidation of SiC-Based Ceramics in Ar-2% Cl₂-O₂ Gas Mixtures at 100°C," *J. Am. Ceram. Soc.*, **75** [7] 1942-48 (1990).
17. J. Hinze and H. Graham, "The Active Oxidation of Si and SiC in the Viscous Gas-Flow Regime," *J. Electrochem. Soc.*, **123** [7] 131066-73 (1976).
18. L. Ogbuji, "Development of Oxide Scale Microstructure on Single-Crystal SiC," *J. Mater. Sci.*, **16**, 2753-59 (1981).
19. M. Maeda, K. Nakamura, and M. Yamqada, "Oxidation Resistance Evaluation of Silicon Carbide Ceramics with Various Additives," *J. Am. Ceram. Soc.*, **72** [3] 512 (1992).
20. T. Narushima, T. Goto, and T. Hirai, "High Temperature Passive Oxidation of Chemically Vapor Deposited Silicon Carbide," *J. Am. Ceram. Soc.*, **72** [8] 1386-90 (1989).
21. D. Mieskowski, T. Mitchel, and A. Heuer, "Bubble Formation in Oxide Scale on Sic," *J. Am. Ceram. Soc.*, **67** [1] C17-18 (1984).
22. J. Costello and R. Tressler, "Isotope Labeling Studies of the Oxidation of Silicon at 1000°C and 1300°C," *J. Electrochem. Soc.*, **131** [8] 1944-44 (1984).
23. S. Singhal and F. Lange, "Effect of Alumina Content on the Oxidation of Hot-Pressed Silicon Carbide," *J. Am. Ceram. Soc.*, **58** [9-10] 433-35 (1975).
24. Z. Zheng, R. Tressler, and K. Spear, "Oxidation of Single-Crystal Silicon Carbide," *J. Electrochem. Soc.*, **137** [3] 854-58 (1990).

25. A. Heuer, L. Ogbuji and T. Mitchell, "The Microstructure of Oxide Scales on Oxidized Si and SiC Single Crystals," *J. Am. Ceram. Soc.*, **63** [5-6] 354-55 (1980).
26. N. Jacobseon, K. Lee and D. Fox, "Reactions of Silicon Carbide and Silicon (IV) Oxide at Elevated Temperature," *J. Am. Ceram. Soc.*, **75** [6] 1603-11 (1992).
27. D. Butt, R. Tressler and K. Spear, "Corrosion of SiC Materials in N₂-H₂-CO Gaseous Environments: II, Durability and Mechanical Properties," *J. Am. Ceram. Soc.*, **75** [12] 3268-77 (1992).
28. A. Bennett, "Requirements for Engineering Ceramics in Gas Turbine Engines," *Mater. Sci. Tech.*, 2895-99 (1986).
29. L. Hinze and H. Graham, "The Active Oxidation of Si and Silicon Carbide in the Viscous Gas-Flow Regime," *J. Electrochem. Soc.*, **123** [7] 1066-73 (1976).
30. K. Luthra, "A Mixed Interface Reaction/Diffusion Control Model for Oxidation of Si₃N₄," *J. Electrochem. Soc.*, **138** [10] 3001-07 (1991).
31. H. Du, R. Tressler, K. Spear, and C. Pantano, "Oxidation Studies of Crystalline CVD Silicon Nitride," *J. Electrochem. Soc.*, **136** [5] 1527-36 (1989).
32. T. Narushima, T. Goto, Y. Iguchi and T. Hirai, "High Temperature Oxidation of CVD Silicon Carbide in Wet Oxygen at 1823 to 1923K," *J. Am. Ceram. Soc.*, **73** [12] 3580-84, 1990.
33. R. Harris and R. Call, "Oxidation of 6H Alpha-Silicon Carbide," in *Silicon Carbide 1973*, pp. 329-36, edited by R.C. Marshal et. al., University of South Carolina Press, Columbia, S.C. (1974).
34. C. Fung and J. Kopanski, "Thermal Oxidation of 3C Silicon Carbide Single-Crystal Layers on Silicon," *Appl Phys. Lett.*, **45** [7] 757-59 (1984).
35. H. Cappelen, K. Johansen and K. Motzfeldt, "Oxidation of Silicon Carbide in Oxyge and Water Vapor at 1500°C," *Acta Chem. Scand. Ser.*, **35**, 247-54 (1981).
36. P. Jorgensen, M. Wadsworth and I. Cutler, "Effects of Water Vapor on Oxidation of Silicon Carbide," *J. Am. Ceram. Soc.*, **44** [6] 258-62 (1961).
37. W. Lu, Steckl, T. Chow and W. Katz, "Thermal Oxidation of Sputtered Silicon Carbide Thin Films," *J. Am. Ceram. Soc.*, **131** [8] 1907-14 (1984).

38. M. Maeda, K. Nakamura and T. Ohkubo, "Oxidation of Silicon Carbide in a Wet Atmosphere," *J. Mater. Sci.*, **23**, 3933-38 (1988).
39. F. H. Horn, "Screw Dislocation, Etch Figures, and Holes," *Philos. Mag.*, **43**, 1210-13 (1952).
40. S. Amelinckx, G. Strumane and W.W. Webb, "Dislocation in Silicon Carbide," *J. Appl. Phys.*, **31**, 1359-70 (1960).
41. E. Buchner and O. Rubisch, in *Silicon Carbide 1973*, p. 428, edited by R.C. Marshall et. al., University of South Carolina Press, Columbia, S.C. (1974).
42. D. McKee and D. Chatterji, "Corrosion of Silicon Carbide in Gases and Alkaline Melts," *J. Am. Ceram. Soc.*, **59** [9-10] 441-44 (1976).
43. N. Jacobson, C. Stearn and J. Smialek, "Burner Rig Corrosion of SiC at 1000°C," *Adv. Ceram. Mater.*, **1**, [2] 154-61 (1986).
44. H.E. Kim and A.J. Moorhead, "Effect of Hydrogen-Water Atmospheres on Corrosion and Flexural Strength of Sintered α -Silicon Carbide," *J. Am. Ceram. Soc.*, **73** [3] 694 (1976).
45. L.O. Hagman and P. Kierkegaard, "The Crystal Structure of $\text{NaMe}_2^{\text{IV}}(\text{PO}_4)_3$ ($\text{Me}^{\text{IV}}=\text{Ge, Ti, Zr}$)," *Acta Chemica Scandinavica*, **22**, 1822-32 (1968).
46. H.Y. Hong, "Crystal Structures and Crystal Chemistry in the System $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$," *Mat. Res. Bull.*, **11**, 173-182 (1976).
47. J.B. Goodenough, H.Y. Hong and J.A. Kafalas, "Fast Na^+ -Ion Transport in Skeleton Structures," *Mat. Res. Bull.*, **11**, 203-20 (1976).
48. D.T. Qui, J.J. Capponi, J.C. Joubert, R.D. Shannon and C.K. Johnson, "Structure Analysis of $\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$ at 300 and 600°C," in *Fast Ion Transport in Solids*, pp. 439-42, edited by Vashishta, Mundy and Shenoy, North Holland, Inc., New York (1979).
49. J.P. Boilot, J.P. Salanie, G. Desplanches and D. Le Potier, "Phase Transportation in $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ Compounds," *Mat. Res. Bull.*, **14**, 1469-77 (1979).
50. R.S. Gordon, G.R. Miller, B.J. McEntire, E.D. Beck and J.R. Rasmussen, "Fabrication and Characterization of Nasicon Electrolytes," *Solid State Ionics*, [3-4] 243-48 (1981).

51. J.J. Brown, D.A. Hirschfeld, D.M. Liu, Y. Yang, T.K. Li, R.E. Swanson, S. VanAken, J.J. Kim, "Ceramic Materials with Low Thermal Conductivity and Low Coefficients of Thermal Expansion," U.S. Patent 5,102,836, April 7, 1992.
52. S.J. Charlton and M.J. Watts, "An Investigation of Thermal Insulation of IDI Diesel Engine Swirl Chambers," *Proc. Instn. Mech. Eng.*, **205**, 263-69 (1991).
53. T. Mani and A. Damodaran, "Aluminum Titanate Powder Synthesis via Thermal Decomposition of Transparent Gel," *J. Am. Ceram. Soc.*, **74** [8] 1807-10 (1991).
54. H. Morishima and N. Ootsuka, "Development of Aluminum Titanate-Mullite Composite Having High Thermal Shock Resistance," *J. Am. Ceram. Soc.*, **69** [10] 1807, C266-77 (1991).
55. F. Parker, "Aluminum Titanate-Zirconium Titanate-Zirconia Composites: A New Family of Low-Thermal-Expansion Ceramics," *J. Am. Ceram. Soc.*, **73** [4] 929-32 (1990).
56. C.J. Brinker and G.W. Schere, ed., *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, pp. 48-53, Academic Press, Inc., San Diego, CA (1990).
57. L.C. Klein, ed., *Sol-Gel Technology for Thin Film, Fibers, Preforms, Electronics and Specialty Shapes*, p. 407, Noyes, Park Ridge, N.J. (1988).
58. *Materials and Components in Fossil Energy Application*, U.S. Department of Energy, Assistant Secretary for Fossil Energy, No. 88, Oct. 1990.
59. R. E. Balzhiser and K. E. Yeager, "Coal-fired Power Plants for the Future," pp. 100-7, EPRI, Edmunds.
60. T. Sato, Y. Kioke et al., "Corrosion and Strength Degradation of Si_3N_4 and Sialons in K_2CO_3 and K_2SO_4 Melts," *Mater. Sci.*, **23**, 1405-10 (1988).
61. J. I. Federer and J. P. Jones, "Oxidation/Corrosion of Metallic and Ceramic Materials in an Aluminum Remelt Furnace," ORHL/TM (1985).
62. J. J. Brown and N. R. Brown, "Durability Testing of Ceramic Particulate Filters under PFBC Conditions," EPRI TR-103286, Project 3161-06, Final Report (1993).
63. T. Sun et al., "Investigation of Long-Term Thermal/Chemical Degradation of Ceramic Filter Materials," Final Report, Center for Advanced Ceramic Materials, Virginia Tech (1993).

64. M. Kang, "Alkali/Steam Corrosion Resistance of Commercial SiC Products Coated with Sol-Gel-Deposited Mg-Doped Al_2TiO_5 and CMZP," Master's Thesis, Dept. of Materials Science and Engineering, Virginia Tech (1994).
65. S. Yang, "Corrosion Resistant CMZP and Mg-doped Al_2TiO_5 Coatings for SiC Ceramics," Master's Thesis, Dept. of Materials Science and Engineering, Virginia Tech (1996).
66. H. Kim and A.J Moorehead, "High-Temperature Gaseous Corrosion of Silicon Nitride in $\text{H}_2\text{-H}_2\text{O}$ and Ar-O_2 Environments," *J. Am. Ceram. Soc.*, **73**, 3007-14 (1990).
67. W. Vaughn and H. Maahs, "Active to Passive Transition in the Oxidation of Silicon Carbide and Silicon Nitride in Air," *J. Am. Ceram. Soc.*, **73**, 1540-43 (1990).
68. H. Du, R.E. Tressler and K. E. Spear, "Thermodynamics of Si-N-O Systems and Kinetic Modeling of Oxidation of Si_3N_4 ," *J. Electrochem. Soc.*, **136**, 3210-15 (1989).
69. D. Cubicciotti and K. H. Lau, "Kinetics of Oxidation of Yttria Hot-Pressed Silicon Nitride," *J. Electrochem. Soc.*, **126**, 1723-28 (1979).
70. D. Cubicciotti and K. H. Lau, "Kinetics of Oxidation of Hot-Pressed Silicon Nitride Containing Magnesia," *J. Am. Ceram. Soc.*, **61**, 512-17 (1979).
71. T.S.C. Singhal, "Thermodynamics and Kinetics of Oxidation of Hot-Pressed Silicon Nitride," *J. Mater. Sci.*, **11**, 500-9 (1976).
72. M. Levy and J. J. Falco, "Hot Corrosion of Reaction-Bonded Si_3N_4 ," *Am. Ceram. Soc. Bull.*, **57** [4] 457-58 (1978).
73. D. S. Fox and N. S. Jacobson, "Molten-Salt Corrosion of Silicon Nitride I, Sodium Carbonate," *J. Am. Ceram. Soc.*, **71** [2] 128-38 (1988).
74. D. S. Fox and N. S. Jacobson, "Molten-Salt Corrosion of Silicon Nitride II, Sodium Sulfate," *J. Am. Ceram. Soc.*, **71** [2] 139-148 (1988).
75. T. Sato et al., "Corrosion of Si_3N_4 in Molten Alkali Sulfate and Carbonate," *Advan. Ceram. Mat.* **2** [3A] 228-31 (1987).
76. D. S. Fox and J. L. Smialek, "Burner Rig Hot Corrosion of Silicon Carbide and Silicon Nitride," *J. Am. Ceram. Soc.*, **73** [2] (1990).

77. G. R. Pickrell, T. Sun et al., "High Temperature Alkali Corrosion of SiC and Si₃N₄," *Fuel Processing Technology*, **44**, 213-236 (1995).
78. M. Ebelmen, C. R. *Acad. Sci.*, **21**, 502 (1845).
79. C. J. Brinker and G. W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, pp 48-58.
80. R. W. Jones, *Fundamental Principles of Sol-Gel Technology* (1989).
81. C. J. Brinker, B. C. Bunker et al., "Structure of Sol-Gel Derived Inorganic Polymers : Silicates and Borates," *Am. Chem. Soc.*, Part II (1988).
82. L. C. Klein and G. J. Garvey, "Effect of Water on Acid- and Base-Catalyzed Hydrolysis of Tetraethylorthosilicate (TEOS) ," *Mater. Res. Soc. Sym. Proceedings*, **32** (1984).
83. K. D. Keefer, "The Effect of Hydrolysis Conditions on the Structure and Growth of Silicate Polymers," *Mater. Res. Soc. Sym. Proceedings*, **32** (1984).
84. C. Sanchez and J. Livage, "Optical Coatings Based on Transition Metal Oxide Gels," *Eurogel '91*, p. 131 (1992).
85. H. Dislich, "Sol-Gel 1984 → 2004 (?)," *J. Non Cryst. Sol.*, **73**, 559 (1985).
86. D. R. Uhlmann, B. J. J. Zelinski et al., "The Ceramist as a Chemist - Opportunities for New Materials," *Mater. Res. Soc. Symp. Proceedings*, **32** (1984).
87. S. Sakka and K. Kamiya, "Glass from Metal Alcoholates," *J. Non Cryst. Sol.*, **42**, 403 (1980).
88. S. Sakka, "Glasses and Glass-Ceramics from Gels," *J. Non Cryst. Sol.*, **73**, 550 (1985).
89. D. R. Uhlmann, "Sol-Gel Activities in the United States, a 1991 Perspective," *Eurogel '91*, p. 3 (1992).
90. J. D. Mackenzic, R. Xu et al., "Ultrastructure Processing of Thin Crystalline Films," *Chem. Proc. Advan. Mater.*, (1992).
91. S. Sakka, K. Kamiya et al., "Sol-gel Preparation and Properties of Fibers and Coating Films," *Am. Chem. Soc.*, (1988).

92. C. J. Brinker, A. J. Hurd et al., "Sol-Gel Thin Film Formation," *Chem. Proc., Adva. Mater.*, (1992).
93. H. D. Megaw, "Crystal Structures and Thermal Expansion," *Mater. Res. Bull.*, **6**, 1007-18 (1971).
94. W. R. Buessem, N. R. Thielke et al., "Thermal Expansion Hysteresis of Aluminum Titanate," *Ceram. Age*, **60** [5] 38-40 (1952).
95. S. J. Charlton and M. J. Watts, "An Investigation of Thermal Insulator of IDI Diesel Engines Swirl Chambers," *Proc. Instn. Mech. Eng.*, **205**, 263-269 (1991).
96. H. Morishuma, Z. Kato et al., "Development of Aluminum Titanate - Mullite Composite Having High Thermal Shock Resistance," *J. Am. Ceram. Soc.*, **69** [10] C-226-27 (1986).
97. W. R. Grace et al., " Al_2TiO_5 - ZrTiO_4 - ZrO_2 Composites: A New Family of Low Thermal Expansion Ceramics," *J. Am. Ceram. Soc.*, **73** [4] 929-32 (1990).
98. T. Woignier, P. Lespade et al., " Al_2O_3 - TiO_2 and Al_2TiO_5 Ceramic Materials by the Sol-Gel Process," *J. Non Crys. Sol.*, **100**, 325-29 (1988).
99. A. V. Prasadaraio, U. Selvaraj et al., "Enhanced Densification by Seeding of Sol-Gel Derived Aluminum Titanate," *J. Am. Ceram. Soc.*, **75** [6] 1529-1533 (1992).
100. H. Wohlfromm, J. S. Moya et al., "Effect of ZrSiO_4 and MgO Additions on Reaction Sintering and Properties of Al_2TiO_5 Based Materials," *J. Mater. Sci.*, **25** 3753-64 (1990).
101. L. O. Hagman and P. K. Kierkegaard, *Acta. Chem. Scand.*, **22**, 1822-32 (1968).
102. D. A. Hirschfeld, D. M. Liu et al., "CMZP - A New High Temperature Thermal Barrier Material," *4th Interna. Symp. on Ceram. Mater. and Comp. for Engines*, Goteborg, (1991).
103. S. Y. Limaye, D. K. Agrawal et al., "Synthesis and Thermal Expansion of $\text{MZr}_4\text{P}_6\text{O}_{24}$ (M=Mg, CA, Sr, Ba)," *J. Am. Ceram. Soc.*, **70** [10] C-232-236 (1987).
104. J. P. Boilot, J. P. Salamie et al., "Phase Transformation in $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ Compounds," *Mater. Res. Bull.*, **14**, 1469-77 (1979).

105. M. Nagai, S. Fujitsu et al., "Ionic Conductivity in the System $\text{NaZr}_2(\text{PO}_4)_3$ - $\text{Na}_3\text{Y}_2(\text{PO}_4)_3$," *J. Am. Ceram. Soc.*, **63** [7-8] 476-77 (1980).
106. R. J. Cava, E. M. Vogel et al., "Effect of Homovalent Framework Cation Substitutions on the Sodium Ion Conductivity in $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$," *J. Am. Ceram. Soc.*, **65** [9] C157-59 (1982).
107. B. E. Taylor, A. D. English et al., "New Solid Ionic Conductors," *Mater. Res. Bull.*, **12** [2] 171-82 (1977).
108. J. B. Goodenough, H. Y. P. Hong et al., "Fast Na^+ -Ion Transport in Skeleton Structures," *Mater. Res. Bull.*, **11** [2] 203-20 (1976).
109. T. K. Li, D. A. Hirschfeld et al., "The Synthesis, Sintering, and Thermal Properties of $(\text{Ca}_{0.6}\text{Mg}_{0.4})\text{Zr}_4(\text{PO}_4)_6$ (CMZP) Ceramics," *J. Mater. Res.*, **8** [11] (1993).
110. D. A. Hirschfeld, T. K. Li et al., "Development of Ultra-Low Expansion Ceramics: CMZP and CMZP composites," Annual Automotive Technology Development Contractors' Coordination Meeting, *Proceedings*, SAE, Inc, Warrendale, Pa., (1992).
111. T.K. Li et al., "Thin Film Coatings of $(\text{Ca}_{0.6}\text{Mg}_{0.4})\text{Zr}_4(\text{PO}_4)_6$ (CMZP) on Si_3N_4 and SiC ," *J. Mater. Res.*, **9** [8] 2014-28 (1994).
112. T.K. Li et al., "Alkali Corrosion Resistant Coatings for Si_3N_4 Ceramics," *J. Mater. Sci.*, **32** (1997).
113. W.M. Russ, "Structure, Property, and Processing Relationship of CMZP- $[(\text{Ca}_{0.6}\text{Mg}_{0.4})\text{Zr}_4(\text{PO}_4)_6]$, Master's Thesis, Dept. of Materials Science and Engineering, Virginia Tech, (1994).
114. S.M. Van Aken, "Thermal Expansion and Thermal Conductivity of $(\text{Ca}_{0.6}\text{Mg}_{0.4})\text{Zr}_4(\text{PO}_4)_6$," Master's Thesis, Dept. of Materials Science and Engineering, Virginia Tech, 43-50, (1990).
115. G. N. Babini et al., "Factors Influencing Structural Evolution in the Oxide of Hot-Pressed Si_3N_4 - Y_2O_3 - SiO_2 Materials," *J. of Mat. Sci.*, **19**, 3487-97 (1984).
116. W. Duckworth, "Discussion of Ryshkewitch Paper," *J. Am. Ceram. Soc.* **36** [2] 68 (1953).