ALKALI/STEAM CORROSION RESISTANCE OF COMMERCIAL SiC PRODUCTS COATED WITH SOL-GEL DEPOSITED Mg-DOPED \textit{Al}_2\textit{TiO}_5 AND CMZP

by

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APPROVED:

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ALKALI/STEAM CORROSION RESISTANCE OF COMMERCIAL SiC PRODUCTS COATED WITH SOL-GEL DEPOSITED Mg-DOPED Al₂TiO₅ AND CMZP

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(ABSTRACT)

The corrosion resistance of two commercially available SiC filter materials coated with Mg-doped Al₂TiO₅ and (Ca₀.₆·Mg₀.₄)Zr₄P₆O₂₄ (CMZP) was investigated in high-temperature, high-pressure (HTHP), alkali-steam environments. Coated specimen properties, including cold and hot compressive strengths, bulk density, apparent porosity, permeability, and weight change, determined after exposure to 92% air-8% steam 10 ppm Na at 800°C and 1.8 MPa for 500 h were compared with those of uncoated specimens. Procedures for applying homogeneous coatings of Mg-doped Al₂TiO₅ and CMZP to porous SiC filters were established and coating of the materials was successfully accomplished. Efforts to stabilize the Al₂TiO₅ coating composition at elevated temperature were successful. Coatings show promise for providing improved corrosion resistance of the materials in pressurized fluidized bed combustion (PFBC) environments as evidenced by higher compressive strengths exhibited by coated SiC specimens than by uncoated SiC specimens following HTHP alkali-steam exposure.
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SECTION 1
INTRODUCTION

Ceramic filter systems are undergoing evaluation for hot gas cleanup in advanced coal-fueled power generation systems. Pressurized fluidized bed combustion (PFBC) technology in particular has received interest as a method of reducing the fuel and emission control costs of coal-fired power generation. The reduction in fuel costs is a result of combined cycle operation, where energy is removed from the combustion gases in a gas turbine before their residual heat is recovered in a conventional steam cycle. The ability of the gas turbine to withstand erosion and corrosion by dust and other contaminants in the combustion gases is critical to the success of the technology. Protection of the gas turbine creates the need for a high temperature, high pressure (HTHP) gas cleanup system between the PFBC and gas turbine. The performance of this system will determine whether it is feasible to operate a gas turbine in such a PFBC combined cycle.

Silicon carbide (SiC) is a prime candidate material for high-temperature gas cleanup systems because of its high fracture strength at elevated temperatures, excellent thermal shock resistance, as well as corrosion resistance in air. Unfortunately, SiC materials are corroded and lose up to 50 percent of their strength in oxidizing environments containing alkalis.\textsuperscript{1} The durability and particulate removal efficiency of candle filters made of SiC are significantly reduced when exposed to an alkali-steam atmosphere.\textsuperscript{1}

Because the compounds Al\textsubscript{2}TiO\textsubscript{5} and (Ca\textsubscript{0.6}, Mg\textsubscript{0.4})Zr\textsubscript{4}P\textsubscript{6}O\textsubscript{24} (CMZP), a new composition developed at Virginia Tech,\textsuperscript{2} possess low thermal expansion, excellent thermal shock resistance, low thermal conductivity, and good corrosion resistance, previous studies were conducted to coat protective thin films of these compounds onto commercially available SiC materials to improve their alkali-steam corrosion resistance at high temperatures.\textsuperscript{3,4} Through the studies, sol-gel
techniques were developed to successfully apply Al$_2$TiO$_5$ coating to dense SiC$^3$ and CMZP coating to dense as well as porous SiC$^4$.

In this project, the sel-gel techniques were further developed to apply Mg-doped Al$_2$TiO$_5$ and CMZP coatings to two commercial SiC candle filters. An analysis of various material properties of coated and uncoated filters before and after exposure to simulated PFBC conditions was performed to determine whether the coatings did indeed improve the alkali-steam corrosion resistance of the SiC candle filter materials.
SECTION 2
LITERATURE SURVEY

Applications of Ceramic Candle Filters

Compared with other high-temperature, high-pressure (HTHP) particulate removal systems, ceramic candle filters are more widely used. They have demonstrated excellent high temperature particulate removal efficiencies, good cleanability, and short-term durability in a variety of high-temperature gas streams. Other gas cleaning technologies require that the gas be cooled prior to filtration, resulting in reduced system efficiency and particulate removal efficiencies of only 65-70%.⁵

To meet turbine equipment requirements in advanced, coal-fueled power generation systems, HTHP particulate control is required.⁶ Particulate removal is also necessary in order to meet strict environmental regulation standards which require the dramatic reduction of all particulates including respirable matter from coal exhaust streams (New Source Performance Standards).⁶

Advantages of the ceramic filter include its capability to withstand variation in the effluent gas stream chemistry, variation in the nature and loadings of the entrained fines, and oscillations in the effluent gas stream temperature and possibly pressure, while maintaining high particulate removal efficiencies, high flow capacity, and relatively low pressure drop flow characteristics.

The disadvantage of a ceramic filter is its short duration due to system upsets or mechanical, chemical, and/or thermal changes in the filter element material.⁷ The problems that occur with a candle filter include blinding of the filter, degradation of the binder material by alkalis, and the loss of the mechanical strength of the supporting tube sheet and subsequent sealing
problems at high temperatures. Candle filters typically lose more than 20% material strength after exposure to HTHP environments. It is suspected that the mechanical strength of the filter elements decreases by weakening of the binder material between the ceramic grains. Candle filters typically fail by radial cracking, with the bottom portion of the filter piece falling to the vessel.  

Currently, efforts are focused on improvement and production of highly durable and reliable ceramic filters. The effects are dependent not only on properties of the material used in the construction of each filter element, but also on the relative stability of that material under aggressive HTHP environments, which contain sulfur, alkali, and chloride phases. Furthermore, manufacturing and production control must be exercised to provide a quality-assured component that meets both design dimensional tolerances and composition criteria, and contains minimal flaw characteristics introduced during production of the filter body. Additional effort is being focused on increasing the strength of the entire non-oxide binder (i.e., glass-phase crystallization), as well as enhancing the corrosion resistance of the binder phase to alkali species.

In selecting a viable, durable filter material, important considerations are modulus of rupture or bend strength, thermal shock resistance, thermal expansion, modulus of elasticity, fracture toughness, thermal conductivity, hardness, density, and potential chemical reactivity. Since many of these material properties are known for dense ceramics but have not been determined for the porous composite structures currently being considered for filter fabrication, ceramic filters have yet to show the durability required for commercial acceptance.

Durability can be improved by developing an optimum processing method and using sol-gel processing for depositing protective thin oxide ceramic coatings. Shape forming techniques are being investigated for certain types of filters. Eventually, as the technology advances and private sector competition develops, the economic factor will become more important.
The compositions of the ceramic candle filters include oxides, mixed oxides, oxide-non-oxide composites, and non-oxide matrices. Silicon carbide-based materials currently dominate the commercial manufacture of ceramic candle filters. Several variations of the candle filter silicon carbide matrix are commercially available. These materials generally contain silicon carbide support grains (500 to 1600 μm) that are held together with an aluminosilicate or clay binder (containing relatively high concentrations of sodium, iron, potassium, calcium, and/or titanium) or a crystallized glass phase. A fibrous aluminosilicate mat or a finer grain silicon carbide layer (80 μm) serves as an outer surface skin to provide a barrier to micron- and submicron-sized particles. Binderless (sintered) silicon carbide can be used in the fabrication of candle filters. These materials appear to contain relatively low concentrations of iron, nickel, and/or chromium within the grain-boundary phase(s).

A ceramic candle filter and system assembly are shown in Figure 2-1. Multiple candle filters are suspended from a metal tube sheet across the pressure vessel through a number of center-bored holes. In most cases, the particulate-laden gas flows from the outside to the inside of the ceramic candle filter, and particles form a cake layer on the external surface. The clean gas is exhausted from above the tube sheet. The particle cake on the external surface of the candle filter is periodically removed by applying a reverse pulse of high-pressure gas.

Typical ceramic candle filters are 1 to 1.5 m long with an internal diameter of 30.5 to 40.5 cm and an external diameter of 50 to 60 cm. The external surface of the candle is composed of a fine porous layer of ceramic fiber, clay, or fine-grain silicon carbide. This fine porous layer provides a surface for forming a particle cake layer and prevents particles from penetrating and blinding the filter element. A coarser inner layer of silicon carbide structurally supports the fine porous layer.
Figure 2-1. Schematic of a candle filter situated in a cleaning module.
Corrosion Behavior of Silicon Carbide

In general, high-temperature alkali corrosion can be categorized by the formation of an alkali compound, incipient melting, and alkali-enhanced oxidation of silicon-based ceramics. For silicon-based ceramics, the oxidation of silicon carbide is governed by oxygen transport through the oxide layer. The oxidation is greatly accelerated when the protective scale (silica) 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.

A study of the reaction of SiC with various gas mixtures and molten salts has been conducted by McKee and Chatterji. Three specific cases for molten salts have been identified. Because of the presence of a stable SiO$_2$ layer between the salt melt and SiC, little reaction takes place for an acidic salt film. However, the protective SiO$_2$ is dissolved and accelerated corrosion occurs for a basic salt film. In an oxygen-depleted melt case, SiO (g) forms at the SiC surface and reacts to form Na$_2$SiO$_3$, resulting in rapid corrosion. McKee and Chatterji exposed pressureless sintered $\beta$-SiC, doped with carbon and boron, to Na$_2$SO$_4$-graphite and Na$_2$SO$_4$-Na$_2$CO$_3$; Na$_2$CO$_3$ melts at 900°C. They observed that 1-g melts of Na$_2$SO$_4$ in crucible tests caused severe corrosion because of the low partial pressure of oxygen at the SiC-melt interface and active oxidation through the formation of SiO vapor.

Blachere and Pettit examined two forms of SiC: chemical-vapor-deposited (CVD) SiC and hot-pressed SiC. Little reaction occurred for the Na$_2$SO$_4$-SO$_3$ films except for SiO$_2$ globules under the sulfate droplets on the CVD material. The hot-pressed SiC exhibited considerable corrosion for the Na$_2$SO$_4$-O$_2$ case. These observations indicated that the protective SiO$_2$ layer was dissolved by the more basic melt.

In a high-temperature air atmosphere, the oxidation reaction rate of SiC is found to be
controlled by a surface reaction product produced by the following reaction:\(^\text{11}\)

\[
\text{SiC} + 2\text{H}_2\text{O} = \text{SiO}_2 + \text{CO}_2. \tag{1}
\]

Water vapor has been shown to accelerate SiC oxidation, and the reaction is considered to progress in two steps:

\[
\text{SiC} + 2\text{H}_2\text{O} = \text{SiO}_2 + \text{CH}_4 \tag{2}
\]

\[
\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2 \tag{3}
\]

The rate-determining step in the reactions is \(\text{CH}_4\) diffusion through the surface product of amorphous \(\text{SiO}_2\).\(^\text{12,13,14,15}\)

Kawakubo et al.\(^\text{11}\) pointed out that an \(\text{SiO}_2\) layer does not seem to be produced nor does it play an important role in the high-temperature water corrosion behavior. But the amorphous \(\text{SiO}_2\) film produced on the surface controls the reaction rate in high-temperature oxidation or hydrothermal oxidation.

When SiC specimens coated with sodium sulfate were exposed to air at 1000°C, Blachere and Pettit\(^\text{10}\) reported that the \(\text{NaSO}_4\) decomposed and the SiC became corroded. Bubble formation and devitrification of protective \(\text{SiO}_2\) scales were observed upon examination of the morphology of corrosion products deposited on the SiC substrate.

The \(\text{Na}_2\text{SO}_4\) hot corrosion of SiC at 1000°C involves the following reactions:\(^\text{16}\)

\[
\text{SiC} (s) + 3/2\text{O}_2 (g) = \text{SiO}_2 (s) + \text{CO} (g) \tag{4}
\]

\[
x\text{SiO}_2 (s) + \text{Na}_2\text{SO}_4 (l) = \text{Na}_2\text{O} \cdot x(\text{SiO}_2) + \text{SO}_3(g). \tag{5}
\]

In the reactions, the evolution of CO and \(\text{SO}_3\) gases causes bubble formation.

Bucher and Rubish\(^\text{17}\) found that siliconized SiC heating elements completely dissolved in a melt of \(\text{Na}_2\text{CO}_3\) after only 5 h at 900°C. Arende and Carran\(^\text{18}\) stated that high dissolution rates, 13 \(\mu\text{m/minute}\) at 1000°C and 60 \(\mu\text{m/minute}\) at 1100°C, occurred in crucible tests of hot-pressed boron-doped SiC in \(\text{CaCl}_2-\text{CaF}_2-\text{CaSO}_4\) melts. The rate was linear with time and exhibited an Arrhenius
relationship with temperature. Excessive corrosion was improved by adding graphite; bubbling in both the melt and liquid scale and a very rough SiC-scale interface were observed. Tressler et al.\textsuperscript{19} stated that Na\textsubscript{2}SO\textsubscript{4} and Na\textsubscript{2}SO\textsubscript{4}-NaCl rapidly corroded SiC at 1000°C, but NaCl melts alone did not react with SiC.

Ferber et al.\textsuperscript{20} studied the effect of powdered coal slag on sintered \(\alpha\)-SiC in air. They found that a cristobalite passivating layer formed after exposures at 1250°C for 24-168 h, and diametral compression c-ring test results showed that strength increases occurred in the \(\alpha\)-SiC specimens. However, dissolution of SiO\textsubscript{2} layers occurred after further exposures, resulting in the formation of Fe, Ni-silicates, and pitting attack. A strength reduction was noted and attributed to the extensive pitting.

Recently, Brown and Brown\textsuperscript{1} studied the degradation of candidate filter materials from various manufacturers in pressurized flue gas containing steam and alkali at 700-850°C. The samples of the materials, including silicon carbide (three brands), mullite, cordierite, refractory concrete, and fibrous alumina-silicate, were exposed in a HTHP test furnace to air containing steam and alkalis. A series of test environments ranged from 8 to 25 percent steam content, and alkali contents of 3.4 to 9 ppm Na, with temperatures ranging from 800 to 850°C and pressures of 1.7 to 1.8 MPa (250 to 260 psi). The exposure period was 500 h, after which the properties of the ceramic specimens were characterized. Overall, their observations suggest that the oxide materials are more durable than SiC in PFBC environments, with the SiC materials losing up to 50 percent of their strength after some exposure tests.

Li et al.\textsuperscript{4} studied the alkali corrosion of silicon carbide following experiments in which commercially available Al\textsubscript{2}O\textsubscript{3}, dense, porous SiC and Si\textsubscript{3}N\textsubscript{4} with 6 wt% Y\textsubscript{2}O\textsubscript{3} (GTE, PY-6) were used. To supplement this study, SiC coated with CMZP and uncoated SiC specimens were also examined. Specimens of SiC were coated with Na\textsubscript{2}CO\textsubscript{3} by dipping heated samples into a saturated
salt solution and placing them in an electric furnace regulated at 1000°C for 50 h. 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 up to 1200°C. However, the presence of sodium with SiC caused dissolution of the SiO₂ protective film and thereby enhanced oxidation. Based on the thermogravimetric analyses and morphology observations on SiC after corrosion by Na₂CO₃, they found that the following reaction mechanisms occurred: Na₂CO₃ decomposed and Na₂SiO₃ formed, oxidation occurred rapidly, forming a protective silica layer below the silicate and a slowing of the reaction, followed by corrosion of the protective silica layer with a repetition of the above steps.

Theories of Sol-Gel Technology

The term "sol-gel" describes chemical processes in which polymeric gels are formed from metallo-organic starting solutions. In recent years, sol-gel processes have shown important advantages for coating a variety of metallic or ceramic substrates to produce superior protective layers. The practice of sol-gel processing is now well-known.²¹

The advantages of sol-gel processing, in general, are: purity of the starting components, homogeneity on the molecular level, and the synthesis of compositions which cannot be obtained through traditional methods. The disadvantages include the high costs of raw materials, large shrinkage which occurs, and the long processing times involved. Research has been focused on the analysis of processing parameters such as precursors, water ratios, solvents, and catalysts. Using these parameters, tailored microstructure can now be obtained routinely.

The most commonly studied sol-gel systems are based on the chemistry of metal alkoxides, M(OR)ₙ. Two key steps are involved in the sol-gel process, hydrolysis and condensation. The reaction can be summarized as follows:
Hydrolysis:

\[ M(OR)_x + H_2O \rightarrow M(OR)_{x-1} + OH^- + ROH \] (6)

Condensation-Polymerization:

\[ 2M(OR)_{x-1} + H_2O + (OR)_{x-1} + M-O-M(OR)_{x-1} \] (7)

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

In general, hydrolysis is facilitated by increases in the charge density on the metal, the number of metal ions bridged by an hydroxo or oxo ligand, and the number of hydrogens contained in the ligand. Hydrolysis is inhibited as the number of hydroxo ligands coordinating M increases. Condensation occurs only by additional reactions when at least one of the reactant species is coordinately unsaturated. Condensation occurs as soon as one OH is present in the coordination sphere of M. This is brought about by adding a base or oxidizing agent to aquo-ions or by adding an acid or reducing agent to oxy-ions.

Acid or base catalysts can influence both the hydrolysis and condensation rates and the structure of the condensed product. Acids can increase the reaction kinetics by producing good leaving groups,

\[ M-OR + H_2O^+ \rightarrow M^+ + :ROH + H_2O, \] (8)

and eliminate the requirement for proton transfer within the transition state.

Alkaline conditions produce strong nucleophiles via deprotonation of an hydroxo ligand:

\[ L-OH + :B \rightarrow L-O^- + BH^+ \] (9)

where L = M or H and B = OH or NH₃. Condensation kinetics are systematically enhanced under basic conditions.

Alcohol is one of the chemical modifications of transition metal alkoxides. Alcohol exchange is a common method of alkoxide synthesis because alcohol exchange reactions occur
readily with metal alkoxide precursors:

$$M(OR)_x + xR'OH \rightarrow M(OR)_{x-4}(OR')_x + xROH.$$  \hspace{1cm} (10)

Alcohol exchange can significantly alter the hydrolysis behavior of transition metal alkoxides.\textsuperscript{21}

The hydrolysis and condensation behavior of the modified precursor depends on the stability of the modifying ligand, which is not always possible to predict on the basis of stability of the parent compound. In general, less electronegative ligands are removed preferentially during hydrolysis, whereas more electronegative ligands are removed more slowly during condensation.

Whether precipitation or gelation occurs depends not only on processing factors of pH gradients, temperature, and speed of mixing, but also on the condensation kinetics. More compact polyanions are formed when the kinetics of condensation via oxolation mechanisms are rapid, whereas slower kinetics result in more open structures and generally allow the formation of clear gels when an acid is added.

The hydrolysis and condensation reactions lead to the growth of clusters that eventually collide and link together into a gel by contact with the substrate and exposure to the atmosphere.\textsuperscript{23,24} The process of gelation can be described as follows: clusters grow by condensation of polymers or aggregation of particles until the clusters collide; then links form between the clusters to produce a single giant cluster that is a gel. The gel network contains a continuous liquid phase, which allows relatively fast transport. The reactions that produce gelation continue long after the gel point.

Most gels are amorphous (noncrystalline), even after drying, but many crystallize when heated. If the objective of the processing is to produce a pore-free coating, it is necessary to heat the gel to a temperature high enough to crystallize the coating. The limitation to this step is the temperature to which the substrate and the film can be subjected. Hermetic films can be achieved in some, but not all, applications.\textsuperscript{21}
Applications of Sol-Gel Technology

Applications for sol-gel thin films and coatings include optical, electronic, and protective films. There are several functions of protective films such as improving corrosion or abrasion resistance, imparting adhesion, increasing strength, and providing passivation or planarization.25,26,27,28

CMZP coatings were applied to SiC and Si3N4 to provide improved alkali corrosion resistance.4 CMZP coatings have near-zero bulk thermal expansion and low crystal anisotropy, adjustability of thermal expansion coefficients from positive to negative by controlling composition and processing parameters, very low thermal conductivity, thermal stability to 1500°C, excellent thermal shock resistance, and good resistance to alkali attack. For the composition (Ca0.7,Mg0.3)Zr4(PO4)9, the thermal conductivity is 0.561 W/mK at 200°C, increasing to only 1.0 W/mK at 1000°C. The thermal conductivity of the composition tends to decrease with increasing Mg²⁺ content.

Al2TiO5 coating to impart alkali corrosion resistance to SiC is attractive³ because of its low thermal expansion characteristics, excellent thermal shock resistance, low thermal conductivity, and good corrosion resistance. The axial thermal expansion coefficients of β-Al2TiO5 along the crystallographic axes a, b, and c are 9.8×10⁻⁶, 20.6×10⁻⁶, and -1.4×10⁻⁶/°C, respectively. The linear thermal expansion coefficient for a polycrystalline β-Al2TiO5 is in the vicinity of 2×10⁻⁶/°C, comparable to that of SiC. The thermal conductivity for polycrystalline β-Al2TiO5 is around 1.5 W/mK, which is substantially lower than the thermal conductivities of most structural ceramics. Therefore, Al2TiO5 ceramic oxide coatings on dense SiC substrates were evaluated and successfully accomplished using sol-gel techniques by other researchers.³

Because alumina coatings provide higher hardness on the surfaces of many substrates, they have been developed in particular for stainless steel.22 A simple application of alumina on a
surface can provide scuff resistance to porous and dense materials. Because ceramics in general have higher hardness than metals and plastics, ceramic coatings have less tendency to become scratched. In the application and adherence of sol-gel alumina coatings on a large scale, some technological problems arise due to thermal expansion mismatches of the coating and substrate materials.

Oxynitride films prepared by nitriding silica gel films are harder than silica alone because they incorporate nitrogen. Gel-prepared oxynitride films incorporate nitrogen in larger proportions than thermally nitrided-conventional films. Both mechanical and chemical durability are developed by these films in hermetic packages for microelectronic devices, where there is a large demand for dielectric films.22

Phosphate coatings were applied to silicate glass panels to improve their chemical resistance to attack by water.22 This process made it possible to make a cheaper window that exhibited the chemical durability of a more expensive window with the use of a small amount of materials. This points out one of the primary advantages of the sol-gel process in the form of films. The added durability of the coating protects the bulk of the material without requiring incorporation of the costly component throughout the material. Mullite, mullite-zircon, and mullite or mullite-zircon with amounts of alumina \( (\text{Al}_2\text{O}_3) \), zirconia \( (\text{ZrO}_2) \), or yttria \( (\text{Y}_2\text{O}_3) \) coatings were plasma sprayed onto a SiC tube. Mullite and mullite-zircon coatings exhibited good thermal shock resistance after 60 thermal cycles in the temperature range of 300 to 1300°C. Although some coatings cracked and spalled due to exposure, the data showed improved corrosion behavior in the coated SiC.29

Protective coatings have many applications. These range from diffusion barriers to limit chemical reactions between matrix and reinforcements during composite fabrication, coatings to control frictional stresses at the interfaces in composites, oxidation or stress corrosion resistant
coatings, non-conducting coatings on conducting substrates, etc. However, a crack-free surface is difficult to achieve for thick coatings because sol-gel films are quite brittle, and relatively high temperatures are required to achieve good properties.\textsuperscript{30,31}

Optical applications include reflective, colored, and antireflective (AR) coatings. Since TiO\textsubscript{2} can alter the reflective properties and palladium (Pd) provides the desired absorption, oxide coatings of IROX (TiO\textsubscript{2}/Pd) on glass substrates have been used as reflective surfaces in construction applications to create reflection and radiation from the outside wall of a building. Selective absorption has been shown to decrease summer cooling costs.\textsuperscript{32} Millions of square meters of optical oxide coatings on glass are produced per year by Schott Glaswerk.\textsuperscript{32} In the SiO\textsubscript{2}-TiO\textsubscript{2} binary system, most of these coatings are single or multi layer interference films. The refractive index of films changes with the composition, microstructure, and porosity. Colored coatings on various substrates can be obtained by change in the absorption of thin film with transition metal oxides.\textsuperscript{33,34} AR coatings have been used as laser damage-resistant coatings for laser optics applications to improve device efficiency. The double layer (TiO\textsubscript{2}-SiO\textsubscript{2}) AR increased the measured cell efficiency by 44%.\textsuperscript{31,35}

There are a number of electronic films. First, there are electrically conducting transparent films for displays. These coatings consist of indium tin oxide (ITO) and cadmium stannate. Second, there are titania films used as photo anodes. Third, there are vanadia coatings deposited on photographic film to reduce static electricity. There are other films such as barium titanate and potassium tantalate used for capacitors, and tungstate films used for electrochromic displays.\textsuperscript{36,37,38}

Two methods are commonly used to prepare coatings by the sol-gel process. The first method involves an application of a precursor solution to a substrate, with subsequent conversion of the precursor to an oxide on the substrate surface. This normally requires water and heat. The second method involves the application of a colloidal suspension, a chemically converted oxide,
to a substrate, with subsequent evaporation of the suspending medium.

Among sol-gel processed materials, thin films are the true leader. Sol-gel-derived thin films have been successfully prepared by dip coating techniques on a variety of substrates, including flat surfaces, fibers, fiber mats, and porous wall tubes. The process is simple. A solution containing the desired alkoxide is prepared with a solvent and water. It is applied to a substrate by spinning, dipping, or draining. A tacky film forms that is typically 1 μm thick, uniform over large areas, and adherent to the substrate. The sol-gel process is useful in applying coatings to complex shapes. The film dries quickly to a micro porous coating of oxide.
SECTION 3
EXPERIMENTAL PROCEDURE

Materials

The SiC substrate materials used in the study were obtained from two commercial ceramic candle filters. Filter one, made by Schumacher Umwelt und Trenntechnik, Germany, is a tube of clay-bonded SiC aggregate with an OD of 60 mm and an ID of 30 mm. Filter two is made by Refractron Technologies, Inc., U.S.A. The candle tube consists of clay-bonded SiC aggregate containing a minimal binder content, and has an OD of 60 mm and an ID of 40 mm.

Specimens of the candle filter to be used for compressive strength and weight change tests were prepared by cutting the filters into slightly concave wedge pieces in a 1:1:2 ratio of width to length to height, respectively, on a trim saw (illustrated schematically in Figure 3-1). The smallest cross section dimensions of the specimens were 10x10 mm if being cut from the Refractron filter, or 15x15 mm if from the Schumacher filter. Care was taken to produce specimens having parallel end surfaces to receive the load from the mechanical testing machine.

Specimens were prepared for permeability (pressure drop) tests by cutting samples from the filters with a minimum face surface area of about 6.5 cm² (1 in.²). Before testing, the specimens were dried in an oven at 110°C for 16 h. The dried specimens were then blown free of dust with clean, dry air. Openings on both sides of a sample were maintained to allow for the passage of air during the test and the rest of the sample was sealed with GE red enamel glyptal paint.

Small pieces cut from the filters were used for bulk density and apparent porosity tests. No special preparation or specimen size requirements were needed.
Figure 3-1. Compressive strength test specimens cut from candle filter wall.
Sol-Gel Coatings

Samples to be coated with Mg-doped Al₂TiO₅ were first washed with deionized water for 30 min in a solid state/ultrasonic (Fisher Scientific FS-14) container, then soaked in 1:1 HNO₃ for 6 h, washed with deionized water, dried at 110°C for 2 h, and finally calcined at 1200°C for 6 h. Samples to be coated with CMZP were first washed with deionized water for 30 min in the solid state/ultrasonic container, then soaked in acetone for 1 h, and dried at 110°C for 2 h. Next, the samples were washed with 10% HF solution, washed with deionized water, dried at 110°C for 2 h, and calcined at 1200°C for 6 h. Finally, the calcined samples were washed in 10% HCl solution, rinsed with deionized water, and dried at 110°C for 2 h.

Solution Preparation

The raw materials for MgₓAl₂₋₂ₓTi₁₊ₓO₅ (Mg-doped Al₂TiO₅) solution were magnesium nitrate hexahydrate (Mg(NO₃)₂•6H₂O), aluminum tri-sec butoxide (Al[C₂H₅CH(CH₃)O]₃), titanium butoxide (Ti[CH₃(CH₂)₃O]₄), ethyl alcohol, nitric acid, and deionized water. The appropriate amounts (Al:Ti:Mg = 1:0.8288:0.0566 in weight ratio) of magnesium nitrate hexahydrate, aluminum tri-sec butoxide, and titanium butoxide corresponding to the composition of MgₓAl₂₋₂ₓTi₁₊ₓO₅ (x < or = 0.2) were first weighed 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. Deionized water required for the hydrolysis reactions of the alkoxides was added last while constantly stirring, and the solution pH was maintained between 1.0 and 4.5. The concentration of the Mg₀.₁Al₁₈Ti₁₁O₅ solution was 2.5 mol/L. The solution was clear with slight green coloration.

The raw materials for CMZP solution were calcium chloride (CaCl₂), magnesium perchlorate hexahydrate (Mg(ClO₄)₂•6H₂O), zirconium propoxide (Zr(C₂H₅O)₄), triethyl phosphate ((C₂H₅O)₃P(O)), hydrochloric acid, ethyl alcohol, and deionized water. The stoichiometric
amounts (Ca:Mg:Zr:P = 1:1.98:27.66:16.31 in weight ratio) 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 2.0 and 4.0 was reached, then zirconium propoxide and triethyl phosphate were added drop by drop. The concentration of the CMZP solution was 0.2 mol/L. The solution was clear with slight yellow coloration.

Viscosity Measurement

Following the preparation of the Mg-doped Al₂TiO₃ solution, the viscosity of the solution was measured according to standard procedures ASTM D445 and D446 prior to dip coating. The viscosity of the MgₓAl₂₋₂ₓTi₁₋ₓO₅ solution was controlled between 1.0 and 6.2 centipoises (cP) by varying the H₂O/alkoxide molar ratio or aging of the solutions. Viscosity measurements for the CMZP solutions were not required.

Coating Techniques

Mg-doped Al₂TiO₃ coating. The pre-treated specimens were immersed in the Mg₀.₁₋₀.₈Al₁₋₀.₂Ti₁₋₁.₁O₅ solution and vibrated for 30 min. The dip coating withdrawal rate was less than 8.0 cm/min, preferably between 2.2 and 4.1 cm/min. The processing flow chart of the MgₓAl₂₋₂ₓTi₁₋ₓO₅ coating is shown in Figure 3-2. The coated specimens were cured in a covered container for 72 h, then heat treated following the schedule presented in Figure 3-3.

CMZP coating. The pre-treated samples were soaked in the boiling CMZP solution for 30 min and remained in the solution while being cooled slowly to room temperature. The samples were withdrawn at a rate of 4-12 cm/min at room temperature. The coated samples were cured at room temperature for 72 h at a relative humidity of 40-80%, followed by air-drying at room temperature for an additional 72 h, and drying at 40-60°C for 48 h, then finally heat treated. The coating processes and heat treatment schedule are shown in Figure 3-4 and 3-5, respectively.
\[ \text{Al[C}_2\text{H}_5\text{CH(CH}_3\text{)O}_3 \ + \ \text{Ti[CH}_3\text{(CH}_2\text{)}_3\text{O]}_4 \ + \ \text{Mg(NO}_3\text{)}_2 \cdot \text{6H}_2\text{O} \]

\[ \downarrow \]

add solution of ethyl alcohol and nitric acid

\[ \downarrow \]

add deionized water

\[ \downarrow \]

adjust pH

\[ \downarrow \]

measure viscosity

\[ \downarrow \]

dip coating

\[ \downarrow \]

heat treatment

---

**Figure 3-2.** Flow chart showing Mg-doped Al\(_2\)TiO\(_5\) coating process.
Room temperature

↓ 1°C/min

65°C for 1.5 h

↓ 1°C/min

100°C for 1.5 h

↓ 1°C/min

150°C for 1.5 h

↓ 1°C/min

250°C for 1.5 h

↓ 1°C/min

350°C for 1.5 h

↓ 1°C/min

450°C for 1.5 h

↓ 10°C/min

1300°C for 10 h

↓ 5°C/min

room temperature

Figure 3-3. Heat treatment schedule for Mg-doped Al₂TiO₅ coated specimens.
CaCl₂ + Mg(ClO₄)·6H₂O
↓
add solution of ethyl alcohol and HCl acid
↓
add deionized water
↓
adjust pH
↓
add Zr(C₂H₅O)₄ + (C₂H₅O)₃P(O)
↓
dip coating
↓
heat treatment

Figure 3-4. Flow chart showing CMZP coating Process.
Room temperature

↓ 0.5°C/min

500°C for 10 h

↓ 5°C/min

1000°C for 4 h

↓ 5°C/min

1200°C for 24 h

↓ 5°C/min

Room temperature

Figure 3-5. Heat treatment schedule for CMZP coated specimens.
Corrosion Test

HTHP test equipment

A schematic diagram of the HTHP test apparatus is shown in Figure 3-6. The 347 stainless steel reaction vessel has an internal volume of 383x10^{-5} m^3. Strength test specimens and additional specimens for other property measurements are placed within the test chamber and separated by thin alumina sheets.

The HTHP vessel is mounted within a high temperature box furnace, secured into place with cut firebrick. The exposed area of the vessel where inlet and outlet piping are attached is surrounded by tightly packed ceramic fiber insulation. The test chamber temperature is constantly monitored using an internal thermocouple. A high pressure liquid metering pump delivers the appropriate amount of NaNO_3 solution of the proper concentration to produce the desired NaNO_3:steam ratio. The steam- and alkali-laden air is introduced to the sample container from one side and travels past the test specimens to the opposite side where it is vented from the vessel. In the exposure test, gas flow rate across the test specimens is maintained at 420 mL/h. Although provisions were not specifically made to force gas to flow through the porous ceramic filter specimens, complete permeation of the gas through the small samples was evidenced in post-exposure SEM examination. The gas leaving the sample container is cooled, passed through a liquid-gas separator, metered, and vented.

Test Procedure

Experimental work consisted primarily of exposing coated and uncoated specimens of two different SiC filter materials to the pressure, temperature, and levels of alkali-steam conditions anticipated to prevail in hot gas clean-up systems of PFBC facilities, followed by post exposure characterization of these test specimens.

In the exposure test run, more than twenty specimens of each filter type, coated and
Figure 3.6. Schematic of the HTHP specimen exposure facility.
uncoated, were positioned in the test chamber. The vessel was heated at a rate of about 100°C/h to the exposure temperature of 800°C. An adjustable pressure regulator dispensed air directly to the sample container from a compressed gas cylinder at the desired pressure. Once the vessel equilibrated at the designated partial pressure of air, total pressure was increased to the desired exposure pressure by pumping water into air line entering the test vessel. This setup generated the air-steam exposure conditions. When pumped into the chamber at a rate such that when the solution vaporized (NaNO₃ decomposes at 380°C), the desired steam and Na concentration (wt% basis) were achieved.

At the termination of the exposure, air and solution delivery was stopped and the vessel was vented of any remaining gases before lowering the temperature at a rate of about 10°C/min.

Evaluation

Properties of SiC candle filter specimens coated with Mg-doped Al₂TiO₅ and CMZP after exposure to the HTHP alkali-steam environment were compared to those of identical, but uncoated, specimens exposed to the same conditions. ASTM guidelines were used to evaluate bulk density, apparent porosity, and room temperature and hot (850°C) crushing strengths.

Room temperature and operating-temperature (850°C) compressive strength determinations were selected for characterization studies for several reasons. The small sample size required for crushing tests compared to other mechanical property test specimens allowed for a greater number of specimens in each exposure tests. This provided for adequate specimens for cold and, most importantly, hot strength measurements, and allowed for statistical analysis of the test results. Also, in general, there is less variability in crushing strength data than in some other mechanical property test data which are strongly affected by surface and other inherent flaws. And lastly, previous work on ceramics in coal combustion environments showed that flexural strength and abrasion-resistance increased whenever compressive strength increased, and vice-versa.39
Compression tests were carried out on an ATS testing machine (model ATS103A06/90 Applied Test Systems, INC.) following ASTM C133-84 guidelines. A head speed of 1.3 mm/min was used in applying specimen loads parallel to the long axis of the bar-shaped specimen. For room temperature tests, corrugated cardboard pieces were used as bedding material, whereas for elevated temperature tests, ceramic wool fiber was the bedding material used. For each filter, eight to ten samples of each treatment were tested to attain one mean cold or hot compressive strength value. The observed differences in average strength values were examined statistically using the Student's t-test at the 99% level of confidence.

Permeability (pressure drop across the sample) was measured using ASTM E128-89 for reference. The prepared samples were attached to the pressure drop test apparatus so that one manometer measured the pressure before entering the sample and a second manometer measured the air pressure after passing through the sample. The differential height of the water in the manometers indicated the pressure drop across the sample. Air flow rate across the specimen was monitored with a flowmeter, and pressure drop was determined at a face velocity of 220 m/h. Three samples of each treatment were measured to obtain an average pressure drop value.

Bulk density and apparent porosity were evaluated following ASTM C20-87 guidelines. Five samples of each type specimen were measured. Weight change was determined by comparing the weight of twenty samples of each type specimen before and after the exposure test.

The phase composition of the samples was identified using the standard X-ray diffraction (XRD) techniques. An X-ray diffractometer (Phillips model PW 1840) with CuKα radiation was used.

The microstructure of the specimens was observed using an environmental scanning electron microscope (ESEM) (Electro Scan Corporation Model E-3). The micro chemical composition of the specimens was analyzed using an energy dispersive X-ray (EDX) detector attached to the ESEM.
SECTION 4
RESULTS

Characterization of Gel-Derived Powders

XRD patterns of the calcined powders derived from CMZP and Mg-doped \( \text{Al}_2\text{TiO}_3 \) gels used for filter coatings are presented in Figures 4-1 and 4-2, respectively. No secondary phase was found in the sol-gel-derived CMZP powders which were calcined at 1200\(^\circ\)C for 24 h. The sharp peaks on the XRD pattern indicate that the calcined CMZP was well crystallized.

The sol-gel-derived Mg-doped \( \text{Al}_2\text{TiO}_3 \) powders were calcined at 1300\(^\circ\)C for 10 h. No phases other than \( \text{Al}_2\text{TiO}_3 \) were detected in the calcined powders. Because \( \text{Al}_2\text{TiO}_3 \) was reported by Parker\(^4\) to decompose into \( \text{Al}_2\text{O}_3 \) and \( \text{TiO}_2 \) between about 800 and 1250\(^\circ\)C, and the SiC filter materials coated with Mg-doped \( \text{Al}_2\text{TiO}_3 \) would be exposed to an alkali-steam environment at 800\(^\circ\)C for 500 h, the sol-gel-derived Mg-doped \( \text{Al}_2\text{TiO}_3 \) powders were heat-treated at 800\(^\circ\)C for an additional 500 h to evaluate the long-term thermal stability of the material at this temperature. Again, no phases other than \( \text{Al}_2\text{TiO}_3 \) were detected in the heat-treated powders. Thus, it was concluded that the addition of Mg\(^{++}\) to \( \text{Al}_2\text{TiO}_3 \) using an Al:Mg weight ratio of 1:0.0566 improves the stability of \( \text{Al}_2\text{TiO}_3 \) and prevents decomposition.

Sol-Gel Coatings

Mg-Doped \( \text{Al}_2\text{TiO}_3 \) Coating

Mg-Doped \( \text{Al}_2\text{TiO}_3 \) coating on the grains of the Refractron and Schumacher SiC filter materials are shown in Figures 4-3 (a) and (b). The coating was applied with a solution having a viscosity of 6.2 cP and using a withdrawal rate of 4.0 cm/min. The EDX analysis of the outer surface and the interior sections of the Refractron and Schumacher SiC specimens confirmed
Figure 4-1. XRD pattern of gel-derived Mg-doped $\text{Al}_2\text{TiO}_5$ powder fired at $1300^\circ\text{C}$ for 10 h.
Figure 4-2. XRD pattern of gel-derived CMZP powder fired at 1200°C for 24 h.
the presence of Al, Ti, and Mg, indicating that the interior open pore walls can also be coated. Figure 4-3 (a) shows a flat, dense, and homogeneous Mg-doped Al\textsubscript{2}TiO\textsubscript{5} thin film covering the grain surface of the Refractron SiC filter material. The film is about 2 µm thick and the grain size of the film is about 1 µm in diameter. The coating adhesion appears to be excellent. Very small cracks were noted on the film, suggesting that the coating technique can be further improved. Similarly, as shown in Figure 4-3 (b), a flat, dense, and homogeneous Mg-doped Al\textsubscript{2}TiO\textsubscript{5} thin film can be seen to form on the grain surface of the Schumacher SiC filter material. The small spherical grains are homogeneous with a grain size of 1 µm. The film thickness is about 2 µm. The coating appears to have good adhesion as shown in Figure 4-4.

It was found that the quality of the Mg-doped Al\textsubscript{2}TiO\textsubscript{5} coating is strongly dependent on the solution viscosity and the withdrawal rate. High viscosity and quick withdrawal rates resulted in cracking of the coated film during subsequent heat treatment. It was found that in order to form crack-free thin film coatings, the viscosity of the Mg-doped Al\textsubscript{2}TiO\textsubscript{5} solution needs to be kept below 6.2 cP and the withdrawal rate can not exceed 8.0 cm/min for viscosity less than 4.6 cP. When the solution viscosity is between 4.6 and 6.2 cP, the withdrawal rate required for a crack-free coating can not exceed 4.1 cm/min. To allow subsequent coating, the Mg-doped Al\textsubscript{2}TiO\textsubscript{5} solution needs to be free from precipitation and/or instant gelation. Solid precipitates tend to cause composition segregation in the solution, and rapid gelation makes a uniform coating impossible.

The heat treatment should include both a low temperature evaporation of water and the organic species generated from the hydrolysis and condensation reactions, and a high temperature crystallization of the Mg-doped Al\textsubscript{2}TiO\textsubscript{5} from its amorphous counterpart. Because cracks usually form during calcination, the evaporation process for Mg-doped Al\textsubscript{2}TiO\textsubscript{5} coating was conducted stepwise from 60 to 450°C with a slow heating rate of 1°C/min. To prevent crystallization of Al\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} prior to the formation of Al\textsubscript{2}TiO\textsubscript{5}, the coated filter specimens were heated directly from 450°C to 1300°C at 10°C/min, and held at 1300°C for 10 h.
Figure 4-3. Scanning electron micrographs showing Mg-doped Al₃TiO₅ coating on filtering surface of (A) Refractron SiC filter material, and (B) Schumacher SiC filter material.
Figure 4-4. Scanning electron micrograph of Mg-doped Al$_2$TiO$_5$ coating on Refractron SiC filter material where the coating adhesion appears excellent.
CMZP Coating

Figures 4-5 (a) and (b) show the best CMZP coating achieved to date on the Refractron and Schumacher SiC grains, respectively. In both cases, a flat, non-homogeneous, and discontinuous thin film is formed on the grain surface. The results presented here suggest that further improvements in the sol-gel technique are required to achieve dense CMZP coatings on the porous SiC filter materials. EDX analysis of the outer surface and the interior sections of the Refractron and Schumacher SiC specimens confirmed the presence of Ca, Mg, Zr, and P, indicating that the interior open pore walls were also coated.

For CMZP coating, the evaporation and condensation processes were conducted with a heating rate of 0.5°C/min from room temperature to 500°C, holding 2 h at 200°C, 300°C, 400°C, 500°C respectively, then rapidly heating from 500 to 1200°C at a rate of 5°C/min, with 4 h holding at 1000°C and 24 h holding at 1200°C. The evaporation process removed all solvent and organic components from the CMZP solution, and the condensation process created a single-phase CMZP coating.

Characterization of Refractron SiC

Results of cold and hot (850°C) compressive strength determinations of the coated and uncoated Refractron SiC specimen following the HTHP alkali-steam exposure are presented in Figures 4-6 and 4-7. The Mg-doped Al₂TiO₅ and CMZP coatings did not affect the cold compressive strength of the Refractron SiC material. However, the data indicate that statistically significant reductions in cold compressive strength occurred in all uncoated and coated Refractron specimens following the alkali-steam exposure. Cold compressive strengths of both coated samples were significantly greater than that of uncoated Refractron SiC filter samples after the alkali-steam exposure.
Figure 4.5. Scanning electron micrographs showing CMZP coating on filtering surface of (A) Refractron SiC filter material, and (B) Schumacher SiC filter material.
Figure 4-6. Cold compressive strength of Refractron SiC filter specimens following HTHP alkali-steam exposure.

**: denotes significant difference in same type samples unexposed and exposed to alkali conditions at 99% confidence level using Student's t-test.

**: denotes significant difference when compared to uncoated SiC exposed to alkali-steam at 99% confidence level using Student's t-test.
Figure 4-7. Hot (850°C) compressive strength of Refractron SiC filter specimens following HTHP alkali-steam exposure.
Likewise, the data show no significant differences in hot compressive strength of either of the coated Refractron SiC samples when compared to that of uncoated specimens. Significant reductions in hot strengths occurred in uncoated and coated SiC specimens following exposure to the HTHP alkali-steam environment. The data show no significant difference in hot compressive strengths of the uncoated and coated samples after the alkali-steam exposure.

Bulk density, apparent porosity, permeability, and weight change data for the Refractron SiC Specimens are summarized in Table 4-1. The data show that, as expected, bulk density of the coated specimens were higher than that of the uncoated filter specimens. Similarly, following the HTHP alkali-steam exposure, bulk densities of coated specimens were higher than that of uncoated SiC. Associated decreases in apparent porosity were also observed for the coated specimens when compared to the uncoated SiC. Permeability of the filters appeared to be unaffected by the coatings for exposed and unexposed specimens. Slight weight gains were registered for all specimens following exposure. No visual evidence of physical deterioration was observed for any Refractron specimens following the HTHP alkali-steam exposure.

XRD analysis revealed the formation of cristobalite in all samples after exposure to alkali-steam, indicating an accelerated passive SiC oxidation process and/or the cristobalite re-crystallization of the low-melting binding phases. Besides cristobalite, a small amount of sillimanite (Al₂SiO₅) was present in the samples after HTHP alkali-steam exposure. It is not clear whether the sillimanite was re-crystalized in the binding phases or the product of the reaction between SiC and Al₂O₃ in the binder.

SEM examination of interior portions of the uncoated specimens revealed that changes had occurred throughout the microstructure of the specimens following the alkali-steam exposure. Figure 4-8 (b) shows the formation of spherical particles of cristobalite on the surface of SiC grains in the exposed, uncoated sample. Figure 4-9 (a) shows the deposition of cristobalite needles on the surface of the SiC grains in an exposed Mg-doped Al₂TiO₅-coated sample. EDX analysis
Table 4-1. Property characterization of Refractron SiC filter material.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Bulk Density (g/cm³)</th>
<th>Apparent Porosity (%)</th>
<th>Pressure Drop (Pa)</th>
<th>Weight Change %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>1.70</td>
<td>43.7</td>
<td>1050</td>
<td>+ 0.39</td>
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<tr>
<td>A2</td>
<td>1.63</td>
<td>44.8</td>
<td>997</td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>1.80</td>
<td>39.0 *</td>
<td>1096</td>
<td>+ 0.46</td>
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<td>B2</td>
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<td>41.8 **</td>
<td>1074</td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>1.86 *</td>
<td>38.0 *</td>
<td>1121</td>
<td>+ 0.54</td>
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<tr>
<td>C2</td>
<td>1.83 **</td>
<td>42.0 **</td>
<td>1110</td>
<td></td>
</tr>
</tbody>
</table>

i:  
A1: As-received.
A2: As-received after exposure.
B1: Mg-doped Al₂TiO₅-coated.
B2: Mg-doped Al₂TiO₅-coated after exposure.
C1: CMZP-coated.
C2: CMZP-coated after exposure.

*: denotes significant difference when compared to as-received samples at 99% confidence level using Student’s t-test.

**: denotes significant difference when compared to uncoated SiC exposed to HTHP alkali-steam at 99% confidence level using Student’s t-test.

‡: denotes significant difference in same type samples in unexposed and exposed to HTHP alkali conditions at 99% confidence level using Student’s t-test.
Figure 4-8. Scanning electron micrographs of Refractron SiC filter material (A) the internal structure of the as-received sample, and (B) formation of the spherical particles of cristobalite on the SiC grains after alkali-steam exposure.
detected the presence of Al, Ti, and Mg. Figure 4-9 (b) shows the CMZP coating on an exposed sample. EDX analysis indicated the presence of Ca, Mg, Zr, and P.

Characterization of Schumacher SiC

The cold and hot compressive strengths of the Schumacher SiC filter material following exposure to the HTHP alkali-steam environment are presented in Figures 4-10 and 4-11, respectively. Generally speaking, the cold and hot strengths of all Schumacher SiC filter samples, were lower than those of their Refractron SiC filter material counterparts.

The data show that the coatings had little effect on room-temperature compressive strength of unexposed Schumacher SiC filter. However, following HTHP alkali-steam exposure, statistically significant reductions in cold compressive strengths of all uncoated and coated specimens were observed. Cold compressive strengths of both coated samples were significantly higher than that of uncoated Schumacher SiC filter samples after the alkali-steam exposure. The cold compressive strength of Mg-doped Al₂TiO₅-coated samples was significantly greater than that of the uncoated as well as the CMZP-coated samples following exposure to the HTHP alkali-steam environment.

On the other hand, the hot compressive strength of unexposed Schumacher SiC samples was affected by both Mg-doped Al₂TiO₅ and CMZP coating procedures. The data show that the uncoated specimens decreased in hot compressive strength as a result of the alkali-steam exposure. However, the alkali-steam exposure did not affect the hot compressive strength of either of the coated specimens. The hot compressive strength of both coated samples was significantly higher than that of uncoated Schumacher SiC filter samples after the alkali-steam exposure.

The results of bulk density, apparent porosity, permeability, and weight change determinations for the Schumacher SiC specimens are summarized in Table 4-2. The data show that, as expected, bulk density of the coated specimens were higher than that of the uncoated filter.
Figure 4-9. Scanning electron micrograph showing exposed Refractron SiC filter material (A) Mg-doped Al₂TiO₃-coated, and (B) CMZP coated sample.
Figure 4-10. Cold compressive strength of Schumacher SiC filter specimens following HTHP alkali-steam exposure.
Figure 4-11. Hot (850°C) compressive strength of Schumacher SiC filter specimens following HTHP alkali-steam exposure.
**Table 4-2.** Property characterization of Schumacher SiC filter material.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Bulk Density (g/cm$^3$)</th>
<th>Apparent Porosity (%)</th>
<th>Pressure Drop (Pa)</th>
<th>Weight Change %</th>
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</tr>
<tr>
<td>B1</td>
<td>1.97</td>
<td>35.2</td>
<td>822</td>
<td>+ 1.69</td>
</tr>
<tr>
<td>B2</td>
<td>1.93 **</td>
<td>37.4 **</td>
<td>797</td>
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<tr>
<td>C1</td>
<td>1.95</td>
<td>35.3</td>
<td>790</td>
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<tr>
<td>C2</td>
<td>1.90</td>
<td>36.7 **</td>
<td>773</td>
<td></td>
</tr>
</tbody>
</table>

i:
A1: As-received.
A2: As-received after exposure.
B1: Mg-doped Al$_2$TiO$_5$-coated.
B2: Mg-doped Al$_2$TiO$_5$-coated after exposure.
C1: CMZP-coated.
C2: CMZP-coated after exposure.

**: denotes significant difference when compared to uncoated SiC exposed to HTHP alkali-steam at 99% confidence level using Student’s t-test.
specimens. Similarly, following the HTHP alkali-steam exposure bulk densities of coated specimens were higher than that of uncoated SiC. Associated decreases in apparent porosity were also observed for the coated specimens when compared to the uncoated SiC. Permeability of the filters appeared to be unaffected by the coatings for exposed and unexposed specimens. Slight weight changes were registered for all specimens following exposure. After exposure to the alkali-steam environment, no visual evidence of physical deterioration was observed for the uncoated and Mg-doped Al₂TiO₅-coated Schumacher SiC samples, except for the CMZP-coated specimens which exhibited a slightly yellowish color. The color change is likely due to a binder phase-CMZP reaction since no color change was observed for the Refractron samples.

XRD analysis revealed the presence of cristobalite in the Mg-doped Al₂TiO₅-coated, and CMZP-coated Schumacher SiC samples, but not in the uncoated samples after exposure to the HTHP alkali-steam environment. However, SEM microscopic examination of the exposed uncoated sample revealed the deposition of spherical particles of cristobalite on the surface of the SiC grains, as shown in Figure 4-12 (b). In the same figure, the binder deterioration due to alkali corrosion can also be seen. Unlike the Refractron SiC filter material, no sillimanite was detected in any of the Schumacher SiC samples. This difference may be due to difference in binder compositions of the two SiC filters.

A SEM micrograph of an exposed Mg-doped Al₂TiO₅-coated sample is shown in Figure 4-13 (a). The formation of spherical particles of cristobalite, 1-4 μm in diameter, on the SiC grains can be clearly observed. EDX analysis detected the presence of Al, Ti, and Mg on the surface of the SiC grains, suggesting that the Mg-doped Al₂TiO₅ coating remains at least partially on the SiC grain surface. Figure 4-13 (b) shows an exposed CMZP-coated sample. EDX analysis indicated the presence of Ca, Mg, Zr, and P on the surface of the SiC grains.
**Figure 4-12.** Scanning electron micrographs of the Schumacher SiC filter material (A) in as-received condition, and (B) after an alkali-steam exposure where binder was deteriorated and spherical particles of cristobalite were formed.
Figure 4-13. Scanning electron micrograph showing exposed Schumacher SiC filter material (A) Mg-doped Al₂TiO₅-coated, and (B) CMZP-coated sample.
SECTION 5

DISCUSSION

Porous SiC filter materials are seriously affected by PFBC conditions as evidenced by their 50-65% reductions in room temperature and operating temperature compressive strengths when compared to as-received samples. Some of the binding phase at the grain interface has melted with the SiC grains to form cristobalite, which will likely cause fracture deterioration of the material with time as cristobalite continues to form in these environments. Also, examination has shown the clay binder in SiC filters to react with alkali, this reaction lowers the liquidus temperature of binder, creating a liquid on the surface. These effects decrease the SiC filter materials strength.

Thin film coatings of Mg-doped Al$_2$TiO$_3$ and CMZP appeared to have no effect on room temperature compressive strengths of unexposed Refractron SiC filters. However, both coated and uncoated specimens showed significant reductions in hot and cold strengths following the HTHP alkali-steam exposure. The room temperature compressive strengths of the coated specimens were significantly greater than that of the uncoated specimens following the exposure. This indicate that the coatings reacted with the binder phase of the filter at elevated temperatures to form a reaction product higher in room temperature strength than the original binding phase. This would be of no benefit to the candle filter at operating conditions.

Thin film coatings appeared to have no effect on room temperature strengths of the unexposed Schumacher filters, but significantly lowered hot strengths of these filters. Although cold and hot strength reductions were registered for all coated and uncoated specimens following the HTHP alkali-steam exposure, strength reductions were significantly less for coated Schumacher SiC specimens.
SECTION 6

CONCLUSIONS

1. Procedures for applying homogeneous coatings of Mg-doped Al₄TiO₃ and CMZP to porous SiC filters were established and coating of the materials was successfully accomplished.

2. Efforts to stabilize the Al₄TiO₃ coating composition at elevated temperatures were successful and a patent application was made.

3. The observations associated with the exposure testing of SiC filter materials to HTHP alkali-steam environments and that Mg-doped Al₄TiO₃ and CMZP coatings show promise for improving corrosion resistance of the materials in PFBC environments.
REFERENCES


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VITA

Min Kang was born in Zunyi, China. She received her B.S. in Chemical Engineering in 1982 from Guizhou Polytechnic Institute, Guiyang, China. In August, 1992, she began graduate studies at Virginia Polytechnic Institute and State University. She completed the requirements for a Master of Science in Materials Science and Engineering in May, 1994.

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