ORNL/Sub/94-SS110/01

*Corrosion Protection of SiC- Based
Ceramics with CVD Mullite Coatings*

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Oak Ridge, Tennessee 37831
Managed by
LOCKHEED MARTIN ENERGY RESEARCH CORP.
for the
U.S. DEPARTMENT OF ENERGY
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Research sponsored by the U.S. Department of Energy,
Office of Fossil Energy
Advanced Research and Technology Development Material Program

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Research sponsored by the U.S. Department of Energy, Fossil Energy Advanced Research and Technology Development Materials Program, DOE/FE AA 15 10 10 0, Work Breakdown Structure Element BU-2

Abstract

SiC based ceramics have been identified as the leading candidate materials for elevated temperature applications in harsh oxidation/corrosion environments. It has been established that a protective coating can be effectively used to avoid problems with excessive oxidation and hot corrosion. However, to date, no coating configuration has been developed that can withstand the rigorous requirements imposed by such applications. Chemical vapor deposited (CVD) mullite coatings due to their desirable properties of toughness, corrosion resistance, and good coefficient of thermal expansion match with SiC are being developed as a potential solution.

Formation of mullite on ceramic substrates via chemical vapor deposition was investigated. Thermodynamic calculations performed on the $\text{AlCl}_3\text{-SiCl}_4\text{-CO}_2\text{-H}_2$ system were used to construct equilibrium CVD phase diagrams. Through process optimization, crystalline CVD mullite coatings have been successfully grown on SiC and Si_3N_4 substrates. Results from the thermodynamic analysis, process optimization, and effect of various process parameters on deposition rate and coating morphology are discussed.

INTRODUCTION

In the recent years, interest has grown in the potential use of ceramics in high temperature engineering applications as a means of increasing operating temperatures and improving efficiencies. For example, the operating efficiencies of heat engines have been improved significantly by using uncooled ceramic components at higher temperatures than those attainable with super alloys. [1] Silicon-based ceramics such as Si_3N_4 and SiC currently appear to be the leading candidate materials due to their unique combination of high strength and thermal conductivity, low thermal expansion, and good high temperature stability. [2] Ceramics possess excellent room and elevated temperature strength as well as thermal stability. However, the brittleness of these materials has limited their usefulness in high contact and structural applications. Some of the potential applications range from structural components in gas turbine and heat engines to hot gas filters. Gas turbines are used in aircraft and in power generation and have been tested for use in automobiles. [3] Potential ceramic components include combustor liners, even turbine blades. Attempts to manufacture valves and piston heads have already been made in internal combustion engines. [4] Ceramics could also be used in heat exchanger tubes in industrial furnaces for glass remelting, steel soaking, and aluminum reclamation. [5]

Need for Coatings

Many engineering operations are conducted at high temperatures in an air or oxygen environment. Oxides unlike most of the carbides and nitrides are typically stable at high temperature in an oxygen and oxygen-nitrogen atmosphere. In case of Si_3N_4 and SiC oxidation does not appear to be a problem due to the formation of a passive SiO_2 surface layer at moderate oxygen pressures. This thin, self-healing layer protects the Si based substrates from catastrophic oxidation by effectively minimizing diffusion of O_2 to the substrate. However, corrosion can occur as a result of the combined effect of the oxygen plus gaseous, condensed, or particulate impurities induced via the gas stream. These impurities can either increase the rate of passive oxidation by modifying the transport rate of oxygen through the protective scale, cause active oxidation via formation of SiO which accelerates the degradation process, or produce compositions such as Na_2SiO_3 which chemically attack the ceramic via rapid corrosion. [6,7] Small quantities of impurities can have a pronounced effect on the corrosion behavior of Si_3N_4 and SiC . This is especially important in applications where heavy residual fuels are being considered. In some cases, strength degradation by as much as 30-45% was observed.

In addition, in gas turbine engine testing, contact stresses were identified as the major cause of damage to structural components made of ceramics such as Si_3N_4 and SiC . The surface damage is attributed to high localized tensile stresses due to bi-axial loading at interfaces resulting from aerodynamic forces and relative motion due to thermal expansion. [8] Tensile stresses are localized at the surface and decrease rapidly inward. These localized stresses may exceed the baseline strength of the ceramic, thus damaging the surface of the component and reducing its strength. This susceptibility to

stress damage could lead to projections that ceramic components, especially under sliding contact may fail unpredictably and prematurely.

Since the eventual failure of these ceramics is mainly due to surface damage, it is proposed that this damage can be reduced via the application of a thin coating that can withstand higher amounts of stresses and is more resistant to corrosion. [9,10] Since the ceramic components are used in high temperature engineering applications, the coating should also possess good adherence, and thermal shock properties.

Coatings to Date

High temperature protective coatings have shown some promise but failed to meet all the requirements of the applications. The coating properties required for a specific application were generally achieved through the selection of material properties and coating process parameters. In general, the desired ceramic properties include low thermal conductivity, a relatively high coefficient of thermal expansion, and most importantly, chemical and mechanical stability in the application environment. Plasma sprayed oxide coatings demonstrated improvements in thermal stress resistance, quite interestingly due to the coating porosity that is characteristically produced by this process. [11] However, the adhesion of these coatings was found to be inadequate. In addition, gas permeability and condensed salt penetration into the porous coating structure may induce coating degradation. Moreover, most state-of-the-art ceramic coating materials, mainly the stabilized zirconias, may also exhibit inherent thermodynamic instability problems when subjected to combustion environments that contain impurities such as sodium, potassium, vanadium, phosphorous and sulfur. Multi-

layered CVD coatings of aluminum nitride and zirconia-toughened alumina ($\text{AlN}/\text{Al}_2\text{O}_3+\text{ZrO}_2$) although extremely adherent, failed at temperatures above 1100°C due to compositional deterioration resulting in coating blistering. [12] Reactions between the ceramic coatings and the corrosive combustion gases or condensates may also cause failure of some coatings. Thus the utilization of ceramic components under stringent conditions mandates not only that coatings be adherent and oxidation resistant, but also that they be chemically stable for extended periods at extremely high temperatures. Recent review papers suggest that further improvements of thermal barrier coatings are still required with respect to corrosion and thermal shock resistance. [10] Diffusion coatings containing mullite as a major phase have shown some promise in thermal cycle tests. Duplex coatings with a mullite inter-layer, and a high alumina content coating on the surface protected SiC from corrosion. [13] High temperature atmospheric plasma sprayed mullite coatings have also shown some promise as corrosion resistant coatings. [14] Although the coatings were unable to completely protect the ceramic under severe corrosion environments, it was evident that the problems were primarily due to the inability of the plasma spray process to produce dense, completely crystalline coatings. Consequently, mullite is identified as an excellent candidate coating material, provided dense crystalline coatings could be produced. Chemical vapor deposition is chosen as a processing technique because of the several underlying benefits associated with the technique.

Chemical Vapor Deposition

The CVD technique is currently used to synthesize a wide range of materials for various applications including solid state devices, wear resistant coatings for cutting tool

applications, oxidation/corrosion resistance applications, thermal shock resistance, monolithic free-standing CVD structures, and for processing microstructurally graded powders. CVD is chosen as the processing technique for many applications primarily because of the superior adherence characteristics of the coatings grown by this process. This is due to the chemical nature of the bonding at the coating/substrate interface as opposed to a mechanical bonding in case of a physical vapor deposition (PVD) process. Additionally CVD also provides the ease and convenience in tailoring the required properties via the control of the microstructure and morphology of the deposit by the control of process parameters and deposition conditions. It also allows for uniform deposition on materials with complicated shapes, cavities, and porosity. [18] Near-theoretical densities are usually achieved due to the atom-by-atom deposition process. It is possible to vary the composition and/or structure of the coating material during deposition, allowing for graded coatings. High temperature materials can be deposited via CVD at temperatures far below their melting points or sintering temperatures. In addition, commercialization of the CVD process is relatively easy as demonstrated by the wide usage in the ceramic cutting tool and wear parts production. However, the CVD process is inherently very complicated and needs to be thoroughly understood in order to synthesize new coatings. The science base available to accurately predict the process attributes for a new CVD process is very limited. Recently there have been attempts to formulate concepts to reduce the ambiguity involved with empirical ways of developing new coatings. [19-21] In addition, since the process requires operation at elevated temperatures, the effects of the high deposition temperatures on the phase stability of the substrate also needs to be well understood. Most importantly, extreme care needs to be taken in handling the toxic and corrosive reactants and byproducts.

RESEARCH APPROACH

Two different approaches were taken in order to obtain the final mullite composition in the coating. A multi-layered system consisting of alternating layers of Al_2O_3 and SiO_2 was investigated since the deposition of Al_2O_3 and SiO_2 is well studied. The second approach was to directly deposit mullite from vapor phase reagents consisting of both Al and Si species. Figure 1 summarizes the various process routes that could lead to the ultimate formation of mullite coating.

Multi-Layered System

Al_2O_3 and SiO_2 coatings were grown using already known precursors used for their deposition commercially on a day-to-day basis. This was done in order to facilitate easy deposition of the coatings, followed by a post deposition treatment via annealing in order to form mullite. Mullite was formed by deKaiser in his diffusion couple experiment of Al_2O_3 and SiO_2 pellets at high temperatures in the range of 1500 °C. [22] The reaction between pressed alumina and silica pellets at 1600 °C has shown the formation of mullite crystals with their c-axis parallel to the direction of diffusion of silica into alumina. This led to crystallites of mullite being oriented perpendicular to the interface.

It was projected that similar results could be obtained by depositing thin alternating layers of Al_2O_3 and SiO_2 , and annealing the coatings to cause diffusion. The overall composition of the coating could be controlled accurately by appropriate selection of the relative coating thicknesses. Initially the multi-layers would have a definite interface with abrupt changes in composition, which can result in great amounts of residual stresses in the multi-layered coating. As the heat treatment step progresses, and the two materials start to participate in the inter-diffusion process, this interface becomes very gradual. The goal was to make sure there are no sharp interfaces, and ultimately to ensure there is complete diffusion across the layers to produce mullite.

The multi-layers were designed to facilitate easy diffusion across the layers. This can be accomplished by growing alumina and silica layers as thin as possible so the diffusion depths that need to be overcome are smaller facilitating complete diffusion across the layers. The thinner layers may result in higher residual stresses in the layers due to the thermal mismatch. There may be an optimum thickness for these layers. Additionally the microstructure of the coating within each individual layer needs to be adjusted so small grain sizes are possible, making grain boundary diffusion more pronounced. The multi-layers will consist of diffusion couples of α - or γ - Al_2O_3 and amorphous SiO_2 . Rate equations will be used in identifying reasonable diffusion times and temperatures to make complete diffusion possible. Care needs to be taken when selecting the diffusion temperature, since it may have a detrimental effect on the substrate. When a mullite layer was formed on a polycrystalline Al_2O_3 via reaction with SiC through formation of SiO, a volumetric increase of 9.7% resulted thus applying compressive stresses on the mullite coating. This information would be very useful in designing the multi-layers. For example, the multi-layers can be designed to achieve functional grading to have compatibility with the substrate on the lower end and

compatibility with the application environment on the upper end. This can simply be done by changing the relative thicknesses of the Al_2O_3 and SiO_2 layers. The final resultant coating would have a pure mullite phase starting from the substrate to a composite of mullite and corundum on the outermost layer.

Direct Deposition

Since there were many difficulties encountered in the multi-layered approach, direct deposition of mullite was attempted. Two different Si donors (TEOS and SiCl_4) were considered along with AlCl_3 , CO_2 , and H_2 . This would be an industrially preferred method for various reasons: i) it would be no longer necessary to monitor the thickness of the individual Al_2O_3 and SiO_2 layers, ii) there would no sharp interfaces after deposition, and iii) the post-deposition anneal step would be totally eliminated. Essentially mullite can be grown in one deposition step.

There are two ways of obtaining the final mullite coating through this route. Deposit mullite directly, or codeposit Al_2O_3 and SiO_2 and anneal the coating to obtain mullite. Control of the composition and the phase of the deposit is important since these factors can have a significant effect on product properties. In the case when mullite is not deposited directly, the diffusion depths will be considerably lower compared to the multi-layered system, and consequently the diffusion times and temperatures necessary will not be as high. The temperature required for complete transformation was expected to be in the range of 1100 °C, based on information from bulk processing.

In the case of direct deposition, it needs to be determined whether the final product is achieved by a direct deposition of mullite from the reactants, or if Al_2O_3 and SiO_2 or an intermediate compound is formed first and then a solid state reaction makes the deposition of mullite possible. Boundary layer effects can influence the way the reactants are transported to the surface based on their density, viscosity, and wetting parameters. Many studies [23] showed that the viscosities of mixed oxides could be several orders of magnitude smaller than that of their individual components.

A true co-precipitation process would involve continued condensation and growth of species with -Al-O-Si- bonds. It is clear however, that reactions leading to -Si-O-Si- and -Al-O-Al- bonds can also occur. In case of hydrolysis reactions, it has been shown that Al tends to hydrolyze faster than Si. It has also been shown that the formation of these species can be controlled by avoiding large excess of water, and also by the addition of a catalyst . [24]

Two different systems were investigated in order to deposit mullite directly in one step. AlCl_3 , CO_2 , H_2 and tetraethoxysilane - TEOS ($\text{Si}[\text{OC}_2\text{H}_5]_4$) mixture and AlCl_3 , SiCl_4 , CO_2 , H_2 mixture. The second mixture turned out to be the viable solution for the direct deposition of crystalline mullite.

EXPERIMENTAL METHODS

The CVD System

A schematic of the CVD system is shown in Figure 2. The reaction chamber is a 5.5 inch diameter vertical reactor made of Inconel 600 alloy, thus providing resistance to thermal shock, yet exhibit a reasonable amount of chemical inertness, which is important in a CVD process. The temperature was maintained by resistive heating coils with a three-zone furnace capable of temperatures up to 1200°C. A pneumatic system provided the convenience of easy switch-over between the furnace and the cooling hood on the reactor. A concentric base-plate allowed the inlet gases and exhaust gases to flow through the bottom of the reactor. The temperature of the base was controlled by water flow. Gases and vapor sources were placed remotely, and were carried into the chamber by stainless steel or inconel tubes depending on the severity of the requirement. The lines were heated when necessary. The flow rates of the gases were precisely controlled with mass flow controllers (1259C, 1461C, MKS Instruments, Andover, MA). Vapor sources were maintained at constant temperatures, and an inert bubbling gas was often used to accelerate the evaporation process. A carrier gas was introduced down stream to quickly carry the vapor to the reactor chamber. Mass flow controllers were often used to control the flow rate of vapors. Chamber pressure was maintained at the desired level by a close-loop controlled pressure controller incorporating a gas ballast in conjunction with a throttling valve before the dry pump. A process controller was also incorporated into the

system. This controller would enable accurate control of the reaction temperature, the source temperatures, gas flow rates, and the chamber pressure.

Materials

The substrates used for deposition were mainly Hexaloy SiC (Carborundum Company, Niagara Falls, NY) and slip cast Si₃N₄ (GN-10, Allied Signal, Torrance, CA). All the substrates were polished bars of 3x4x20 mm size. The substrates were placed "standing-up" at various levels in the reactor in order to study the deposition characteristics at different distances from gas entry. The different gases and chemicals used in the experiments were:

Chemical	Form	Supplier	Purity
Hydrogen	Gas	Matheson	99.997
Argon	Gas	Wesco	99.999
Chlorine	Gas	Matheson	99.96
HCl	Gas	Matheson	99.99
Carbon Dioxide	Gas	Airco	99.999
Silicon Chloride	Liquid	Strem	99.995
TEOS	Liquid	Strem	99.99
Aluminum	Solid	ALCOA	99.9

X-Ray Diffractometry

X-Ray diffractometry was performed on a Nicolet I2 diffractometer with a Cu x-ray tube and a Ni filter resulting in a Cu Ka radiation. The X-ray beam width was maintained at 2.5 mm. The unit was run at a standard voltage of 40 KV and a standard current of 20 mA. At this voltage and current level, the X-rays were estimated to penetrate an average depth of 50 μm , thus covering not only the depth of the coating, but also part of the substrate. Thus, all the diffraction data also contained substrate information. Typically angles of 2θ from 90 to 10 degrees were scanned at the rate of .04 degrees every 2 seconds. The 2θ and ω angles were driven by stepper motors controlled by Falcon microprocessor. Smaller steps and longer times were used when slower scans were necessary in order to obtain a higher resolution. The specimens were mounted on polymer disks, and a sample spinner was used to rotate the samples while scanning in order to average out any orientation effects in the coating/substrate combination. A high purity silicon standard was used as a reference for calibration throughout the work. The diffraction data was collected in a MicroVax II computer with graphic attachment and printed in the form of 2θ angles vs. X-ray intensity. Specific peaks were marked for d-spacings and relative intensity. The X-ray diffraction patterns were compared to the values listed in the JCPDS diffraction file.

Scanning Electron Microscopy

The coatings were examined in a JEOL JSM6100 scanning electron microscope (SEM). The samples were mounted on aluminum or copper stubs and usually sputtered

with gold to obtain conductivity on the surface. A Hummer VI-A sputter coater was used. They were also often coated with carbon with a Cressington 108 Carbon/A evaporator. While taking cross section micrographs samples were usually viewed at 90 degrees, or tilted to a 15 degree angle. Micrographs were usually either digitized and printed on thermal paper, or instant photographs were taken using a Polaroid attachment. The microscope was also equipped with a Kevex X-ray energy dispersive spectroscope (EDS) and a detector attachment. The output was processed, normalized for background, and printed as spectra corresponding to the elements. Penetration depth in the silicon based ceramics was estimated at approximately 1 μm for a voltage of 5 to 10 kV. Quantitative analysis for elemental composition was performed on a computer attachment.

Transmission Electron Microscopy

To better understand the structure, defects, the inter-diffusion between the layers, as well as the coating/substrate interface, transmission electron microscopy (TEM) was necessary. In order to produce electron transparent cross-sections, coated samples were cut on a Buehler[®] Isomet low speed diamond saw. The cross-sectional samples were produced by gluing two films face-to-face, resulting in a "sandwich". The samples were glued to a 3 mm copper grid with epoxy, followed by grinding, polishing, and dimpling in the usual fashion. The dimpled samples were ion-milled in a Gatan Duomill, using a 5 kV source at 8-10 ° incidence angles. Special care was taken to avoid irradiation damage during ion milling by milling at low angles and by cooling the sample using liquid nitrogen. The samples were studied in a JEOL 200CX TEM operated at 200 kV.

Chemical analysis of the films was carried out in a VG HB603 scanning transmission electron microscope (STEM).

Metallography

Samples were mounted in bakelite phenolic. In case of cross-section mounting, diallyl phthalate was used for edge retention. The samples were also often nickel plated to avoid edge-rounding. The mounted specimens were ground and polished with diamond impregnated wheels and diamond slurry. A Struers automatic polisher was used. The mounts were loaded on the sample fixture and first ground with 40 and 20 μm diamond wheels. 300 rpm wheel speed with wheel and sample spindle spinning in opposite direction was used for this step. 200 N load was used during grinding. Samples were then polished with 15, 6, 3, and 1 μm diamond suspension on Petrodisks at 150 rpm and 100 N load. The samples were also etched with 10% HF solution in order to evaluate the crystalline nature of the mullite coating.

Oxidation and Corrosion Analysis

Preliminary high temperature testing of the layered samples has been performed at 1200, 1400 and 1600 $^{\circ}\text{C}$. A 4 inch diameter Al_2O_3 tube furnace was used. The samples were placed in Al_2O_3 boats and were heated to the temperature and cooled at reasonably fast rates (Up to 1000 $^{\circ}\text{C}$ a minute). So, the samples also have a reasonable amount of thermal shock inherently put in them. The annealing tests were performed in a positive argon atmosphere, and the oxidation tests were done in static air.

All oxidation experiments were performed in a Lindberg horizontal tube furnace with MoSi₂ elements capable of temperatures up to 1700 °C. There was approximate hot zone of 12 inches. A 4 inch mullite tube was used to house the samples. The ends were capped with refractory flanges. Samples were usually mounted in an alumina boat and moved to the middle of the hot zone.

Corrosion resistance evaluation was performed at Oak Ridge National Laboratory. Mullite coated Si₃N₄ samples were typically loaded with Na₂SO₄ in the liquid form while being heated to approximately 200 °C. The specimens were typically loaded with about 5 mg/cm² of Na₂SO₄. Corrosion experiments were conducted for up to 100 hours at 1000 °C and 101 kPa. The Na₂SO₄ loaded specimens were placed on an Al₂O₃ holder and exposed to a flowing oxygen environment (200 cm³/min) in a quartz tube heated by an electric resistance furnace. The resulting specimens were mounted in epoxy and polished to examine corrosion products and resulting surface microstructures. A JEOL Superprobe 733 electron microprobe analyzer (EMPA) equipped with wavelength dispersive spectrometer and an energy dispersive spectrometer (EDS) were used for morphology characterization and phase identification. Further details of the corrosion testing procedure are described elsewhere. [25]

Micro and Macro Scratch Test

Two types of scratch tests were used to characterize the adhesion of the coatings. While the Macro scratch test gives a quick value of the adherence without much preparation of the sample involved, it was shown that it is not a true measure of coating

adhesion, since it takes into account such factors as surface friction. [26] However, the test was believed to be useful for quality control purposes through an indication of the coating durability. The micro scratch test eliminates some of the problems associated with macro scratch test and gives a better indication of interfacial adhesion, but requires that the sample be metallographically polished in cross section. One frequently observed problem in this process is the edge-rounding of the coating during polishing, causing errors in adhesion measurement. Both the tests yield a critical load L_c , which is used as a measure of adhesion.

In Macroscratch test, scratch testing with a Rockwell[®] C diamond indenter was used. The test was performed with continuously increasing normal load (typically in the order of several Newtons) until the onset of coating removal from the substrate. This is detected with an acoustic emission detector mounted on top of the indenter. A load cell measures the load as the indenter traverses. The load at which the coating debonds from the substrate is called the critical load. This value is used as a measure of the work energy or shear stress required to debond the coating, and therefore used as an indication of its adherence.

The Microscratch test [26, 27] encompasses scratching a metallographically polished surface of the sample normal to the coating/substrate interface, exposing a portion of the interface-substrate-coating. A modified microhardness tester (Tukon - Wilson Instruments) equipped with an Oriel motorized micrometer was used for testing. The indenter was fixed, while the sample stage was driven with the micrometer. A scratch is generated generally perpendicular to the interface via a diamond indenter. A Knoop indenter was used with its long axis aligned parallel to the direction of scratching. The scratch was applied starting from the substrate towards the coating. Variations

include scratching at an angle to the interface, and scratching from the coating towards the substrate. The scratching steps were repeated with increasing normal loads until the onset of crack formation at the coating/substrate interface. Several scratches were made at various loads, and the samples were examined in the SEM. The load at which the coating debonds from the substrate is termed as the critical load. This value is used as a measure of the work energy or shear stress required to debond the coating, and therefore an indication of its adherence.

RESULTS AND DISCUSSION

This section is divided into seven parts. Results from the multi-layered approach are discussed in the first part. Direct deposited system with TEOS precursor is discussed in the second part. Results of the extensive thermodynamic equilibrium calculations for the $\text{AlCl}_3\text{-SiCl}_4\text{-CO}_2\text{-H}_2$ direct deposition system for mullite are discussed in the third part. In the fourth part, results from the thermodynamic analysis are correlated with the deposition variables to evaluate the possible rate-limiting mechanisms. In addition, composition, morphology, and crystallographic orientation of the mullite coatings are also discussed in this section. In the fifth section, the solid solubility range of mullite when produced by CVD is discussed. In the sixth and seventh sections, results from adhesion and corrosion resistance evaluation of mullite are discussed.

Multi-Layered Coating System

Multilayers of $\alpha\text{-Al}_2\text{O}_3$ and vitreous SiO_2 were grown on SiC and Si_3N_4 substrates by CVD. The CVD reactor was modified so that the alternating layers could be deposited using the same fixturing without having to take the sample out of the reactor. The thickness of the layers was adjusted such that the overall composition of the coating was that of stoichiometric mullite. The reactant gas concentration and time

between changeovers was used to obtain the desired composition of the overall coating. The one problem that was anticipated with this approach is that the interfaces between layers were of abrupt changes in composition and could lead to mismatch problems.

SiO₂ was deposited by the pyrolysis of Tetraethoxysilane (Si[OC₂H₅]₄) resulting in amorphous coatings. The deposition reaction was carried out at 800 °C at 50 torr pressure. The chemical reaction is as follows : [28]

Tetraethoxysilane (TEOS) was bubbled from a constant temperature Inconel container kept at 100 °C. Typically 25 cc of Ar was used as the bubbling gas, and the vapor was carried to the chamber with approximately 2 liters of Ar through heated 316 stainless steel tubes. Vapor pressure curves of TEOS in conjunction with the bubbler temperature and bubbling and carrier Ar flow rates were used in order to estimate the amount TEOS being introduced into the chamber. Growth rates were typically in the order of 1 μm per hour. The SiO₂ layer was amorphous and had a globular morphology. The coating was also dense and uniform in thickness.

Al₂O₃ coatings were grown on Si₃N₄ and SiC substrates in a reactor geometry that was also suitable for depositing SiO₂. Process parameters used for depositing Al₂O₃ were varied within the range established for SiO₂. The reactor geometry and process parameters had to be adjusted so as to accommodate both SiO₂ and Al₂O₃ coatings. In-situ formed AlCl₃, and H₂O formed by the water-gas-shift reaction of H₂ and CO₂ were used as the reactants in formation of Al₂O₃. An external generator was used to produce

AlCl₃ vapor by placing aluminum chips in an inconel tube in a tube furnace and flowing H₂ and Cl₂ gases over them. Several condensation problems were encountered in transporting the vapor from the source to the chamber because the vapor had to pass through the cold reactor base. These problems were overcome with better handling of the vapor, changes in base fixturing, and efficient control of the base temperature. An internal generator housed at the lower end of the vertical reactor eliminated the condensation problems, but did not provide the independent control of the temperature of the Al chips, since the temperature of the Al chips was defined by the hot wall reactor temperature in the lower region. The external AlCl₃ generator was maintained at 325 °C. Cl₂ is usually carried through the generator with a low flow rate Ar carrier. The generator was very effective and resulted in 100% conversion efficiency. This was confirmed by weighing the Al chips at the beginning and end of every experiment. For example, for a Cl₂ flow rate of 15 sccm, a weight loss in the Al chips of 1.35 g was observed, which is close to the theoretical value of 1.3692 g.

The underlying chemical reactions for the formation of Al₂O₃ by the hydrolysis method are as follows:

The water-gas-shift reaction is the most important and potentially rate-limiting reaction in the formation of Al₂O₃ and has been shown to be important in controlling the

thickness and structure of the deposit accurately. Growth rates were in the order of 0.5 μm per hour. The resulting alumina coatings had a corundum(α) structure. This agrees generally with the known phase transformation characteristics of amorphous Al_2O_3 as a function of temperature, [29] although formation of phases by CVD need not necessarily be in agreement with trends in the conventional processes.

Layered coatings with overall thicknesses of 1 to 1.5 μm were grown on SiC and Si_3N_4 substrates. Since the mismatch in thermal expansion coefficient between Si_3N_4 and SiO_2 , and Si_3N_4 and Al_2O_3 is of the same magnitude, both the configurations of SiO_2 being the inter layer with Al_2O_3 being the outer layer and vice-versa have been tried. Since a layer of SiO_2 is always expected to be naturally present on the Si based substrates, it was believed that there may be an advantage with using SiO_2 as the inter-layer. Figure 3 shows $\text{SiO}_2/\text{Al}_2\text{O}_3$ layered coating on a Si_3N_4 substrate with the line scan images showing the amount of Si and Al present across the coating/substrate interface.

The multilayered coatings were annealed at different temperatures in order to facilitate the formation of mullite via interfacial reactions. The annealing was performed in a positive Ar atmosphere in order to prevent oxidation from the environment. Initially an annealing temperature of 1200 $^{\circ}\text{C}$ was chosen. No significant change was observed in the coating morphology or the interfacial characteristics of the coatings on both Si_3N_4 and SiC substrates. X-ray analysis performed on these coatings before and after annealing showed no detectable phase changes in the coating. Figure 4 shows the X-ray diffraction pattern of the multi-layered coating after heat treatment showing pure α - Al_2O_3 peaks in the coating and no transformation. A small diffusion zone was observed between the Al_2O_3 and SiO_2 layers. Figure 5 is a TEM micrograph of an Al_2O_3 - SiO_2 interface after a 2 hour anneal at 1200 $^{\circ}\text{C}$, showing the presence of a 50 nm reaction zone

between the pure SiO_2 and pure Al_2O_3 regions. Chemical analysis of this reaction layer in the STEM using a 1 nm electron probe showed the formation of a compound in which the Al:Si atomic ratio was measured to be 65:35 (see EDS spectra in Figure 5) which is close to the theoretical ratio in stoichiometric mullite. This coating exhibited no visible signs of cracking upon cooling. The diffusion zone, however was not large enough to cover the entire coating cross-section. In other words, there were large portions of pure Al_2O_3 and pure SiO_2 layers that did not exhibit any inter-diffusion.

In order to widen the diffusion zone, the temperature of the post deposition anneal was increased to 1350 °C. This treatment resulted in the delamination of the Al_2O_3 layer. TEM micrograph (Figure 6) of this sample shows partial transformation of the amorphous SiO_2 layer immediately next to the Al_2O_3 coating into crystalline silica. Cracks were observed at the crystalline SiO_2 layer and Al_2O_3 interface indicating that phase transformation may be responsible for coating delamination. These results have led to projections that transformation of amorphous SiO_2 is the reason that most of the coatings developed on Si based substrates exhibit poor adhesion. It is therefore felt that for any coating configuration to maintain adherence at elevated temperatures on Si based substrates, it is essential that this problem be addressed. It was necessary to understand the amorphous to crystalline transformations in coatings under CTE mismatch and growth stresses.

To quantify the dependence of devitrification on pressure and temperature, experiments were conducted on bulk silica powders. The degree of transformation was found to be dependent on the pressure, and further to increase with an increase in pressure. Figure 7 shows the {101} peak of α -cristobalite for various pressures at 1270 °C. Similar trend was observed at other temperatures. Almost 100% transformation was

observed at 1360 °C even without any pressure. Monolithic SiO₂ coatings were grown on SiC in order to perform comparative studies. The samples were hot pressed in a similar fashion in order to identify the extent and location of devitrification, and the extent of cracking both in the coating and at the interface. As for the dependence of transformation on pressure, the opposite trend compared to the bulk powders was observed. The formation of cristobalite was inhibited by the application of external pressure in coatings. Crack formation was observed at the very point of crystallization of the coating. In all observations, transformation occurred at the point of higher tensile stress within the coating. Details of this work were presented elsewhere. [30]

Vitreous to crystalline transformation in silica led to coating spallation due to cracking caused by volume changes. The transformation was affected by stresses within the coating. Stresses that aid volume contraction in silica enhanced transformation, while those that aid volume expansion inhibited transformation. It was concluded that the multi-layered approach to form mullite coatings was not viable since very high temperatures were needed in order to facilitate reasonable diffusion between Al₂O₃ and SiO₂ layers. Furthermore, the high temperature treatment causes transformations within the coating leading to failure before any considerable diffusion can take place.

Performance

Although the multi-layered coatings did not facilitate formation of mullite, they performed better than uncoated ceramic substrates to certain temperatures. Preliminary high temperature testing of these samples was performed at 1200, 1400 and 1600 °C in static air. The samples were placed in Al₂O₃ boats and were heated to the set

temperature and cooled at relatively fast rates (approximately 1000 °C a minute), inherently inducing a reasonable amount of thermal shock. In all the coating configurations tested, no major damage to the coatings was observed up to 1200°C on Si₃N₄ substrates, and up to 1400 °C on SiC substrates for short times. X-ray analysis performed on these coatings before and after the testing showed no phase change in the coating.

TEOS+AlCl₃+H₂+CO₂ System

Thermodynamic calculations were used to determine limiting criteria for the co-deposition of SiO₂ and Al₂O₃ from TEOS-AlCl₃-CO₂-H₂ mixtures and aid in establishing rate-limiting gaseous species. Additionally, this information was used to help determine the range of input conditions which would produce SiO₂ and Al₂O₃ at equilibrium. Relative proportions in concentrations of the reactants necessary (Si[OC₂H₅]₄, and AlCl₃) to deposit SiO₂ and Al₂O₃ were varied over a set of temperatures (800, 900 and 1000 °C) and pressures (50 and 100 torr). CVD phase diagrams were constructed by varying the concentration of AlCl₃ over a range of 0.1 to 1.5 moles and that of Si[OC₂H₅]₄ over a range of 0.1 to 0.4 moles. Figure 8 shows the CVD phase diagrams generated using these set of conditions.

The phase diagrams indicate that SiO₂ and Al₂O₃ can never form simultaneously for any of the input conditions. However, compounds such as Al₂SiO₅ are formed along with Al₂O₃ and SiO₂ at different conditions. It was also found that Al₂O₃ and SiC may be formed simultaneously over a range of input conditions and reactant concentrations. These phases may be used as an intermediate layer in the cases when SiC is used as a

substrate. The calculations also suggest that multi-layers of aluminosilicate compound (Al_2SiO_5) with either Al_2O_3 or SiO_2 can be deposited with the same input conditions by varying the concentration of the reactant species. Thickness of these layers can be adjusted to obtain the overall relative proportions of Al_2O_3 and SiO_2 necessary to form mullite.

Coating Morphology and Al/Si Ratios

It was projected that the absence of a sharp interface and the gradual change in the thermal expansion coefficient would decrease the residual stresses and improve adherence by avoiding interfacial cracking. The composition of the codeposited coating was successfully varied by varying the proportions of the individual reactants necessary to grow monolithic Al_2O_3 and SiO_2 coatings. For example this was achieved by varying the temperature of the TEOS bubbler, in effect varying the amount of TEOS entering the chamber.

Successful deposition of Al_2O_3 in the same reactor geometry used for SiO_2 deposition enabled the codeposition of SiO_2 and Al_2O_3 . Reactant concentrations and process parameters were adjusted to control composition, specifically the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio. Energy Dispersion Spectra and Quantitative Analysis were performed to determine these ratios. The acceleration voltage of the filament in the scanning microscope was selected so as to reduce the influence of substrate material. A variety of process conditions were investigated to find their influence on the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio in these coatings.

Figure 9 shows the energy dispersion spectra and quantitative analysis performed on three samples that were grown with increasing amounts of TEOS. Peaks corresponding to Al and Si were observed throughout the coating. The relative proportions of the constituent materials were calculated by normalizing the atomic percent to 100. The gold present in the spectra is the conductive coating on the samples. The increase in Si content in the coatings is very evident from the spectra. The Al:Si ratio is approximately 5:1 in one case, versus 3:2 in the other. The acceleration voltage of the filament in the scanning microscope was selected so as to reduce the influence of substrate material. To verify this effect Al_2O_3 coatings were grown on WC-Co substrates. Only Al in the coating and Au in the conductive coating were detected. This confirmed the fact that the substrate material had no effect on the energy dispersion spectra at the chosen filament voltage. It was also observed that SiO_2 is the dominant growth species in the codeposited system. Thermodynamic analyses also indicate this trend. It was also known that growth rate of SiO_2 as a single phase coating is in the order of 1 μm an hour as opposed to 0.5 μm for monolithic Al_2O_3 . X-ray diffraction analysis of the substrate/coating system showed no peaks related to the coating, indicating that the coatings were amorphous. It is believed that SiO_2 is formed via the pyrolysis of tetraethoxysilane, and AlCl_3 takes the available oxygen from the TEOS byproducts and readily forms the oxide thus not taking oxygen from water-gas-shift reaction to form a crystalline deposit. Other variations to this coating configuration such as constant Al_2O_3 deposition with intermittent introduction of TEOS were attempted but essentially resulted in amorphous deposits.

SiCl₄+AlCl₃+H₂+CO₂ System

Equilibrium Thermodynamic Analysis

Several calculations were performed on the AlCl₃-SiCl₄-CO₂-H₂ system at different process parameters at each set of deposition conditions. Some additional calculations were also performed by substituting AlCl₃ and SiCl₄ with AlBr₃ and SiBr₄, and AlF₃ and SiF₄. Table 1 summarizes the different process conditions that were chosen for calculations. The amount of individual species (both gaseous and condensed) from the computer output is used to generate the CVD phase diagrams. These diagrams represent, for a set of reaction conditions, and input reactant concentrations, all the possible phases that would be present at equilibrium. The reaction that yields mullite from AlCl₃ and SiCl₄ is assumed to be as follows:

Figure 10 shows a ternary CVD phase diagram of AlCl₃-SiCl₄-CO₂-H₂ system at 1000 °C and 75 torr. The ratio of H₂:(AlCl₃+SiCl₄+CO₂) was maintained at 5:1. Since the concentration of H₂ was fixed at 500 moles, the total moles of AlCl₃+SiCl₄+CO₂ was 100. As one would expect, Al₂O₃-based products form along the AlCl₃-CO₂ line, and SiO₂-based products form along the SiCl₄-CO₂ line. Pure oxides form at high CO₂ concentrations, oxides+carbon in the medium CO₂ concentration, and oxides+carbides in the low CO₂ concentration. To avoid carbon in the deposit, operating in the regime where there is excess CO₂ available for the reaction is necessary. Excess carbon towards the left portion of the diagram is a result of the lack of availability of O₂ in the reaction to

form the gaseous byproduct, CO. According to the phase diagram, pure mullite can only be obtained as a line compound, between the mullite+Al₂O₃ and mullite+SiO₂ regions. Since Gibbs free energy of formation of SiO₂ is lower than that of mullite, which is lower than that of Al₂O₃, all the oxygen available is first used to form SiO₂, then mullite, and then Al₂O₃.

Based on the CVD phase diagram (Figure 11), reactant gas composition of AlCl₃ and SiCl₄ were varied (mole fractions from 10⁻⁵ to 1) keeping the CO₂:H₂ ratio at 1:2 to narrow the composition range. The resulting phase diagram (Figure 11) shows that mullite can be obtained with these starting reactants if the stoichiometry of AlCl₃:SiCl₄ is maintained at the same level as that of mullite (Al:Si = 3:1). It should be noted that theoretically, any deviation from this input stoichiometry results in excess Al₂O₃ or SiO₂. However, it is projected that mullite will have a range of solid solubility when produced via CVD, as shown with the shaded region in Figure 11. Since excess SiO₂ in mullite is detrimental to elevated temperature properties of these coatings, it is critical to ensure that no residual SiO₂ is obtained. This can be easily achieved, as indicated by the CVD phase diagram by shifting the input reactant stoichiometry slightly to the Al rich side.

Effect of Temperature

Temperature was varied from 800 °C to 1200 °C in steps of 200 °C. The results are shown in the CVD phase diagrams in Figures 12. When the temperature was reduced to 800 °C, the formation of mullite was not predicted. Instead, sillimanite (Al₂O₃•SiO₂) is formed in the high CO₂ concentration range. At 1200 °C, many phases that were present at 1000 °C (Figure 13), including carbon were absent throughout the phase

diagram. Based on the analysis of output gas stoichiometry at 1200 °C, gaseous products such as CH_4 were formed, rather than formation of carbon as a solid deposit. At this temperature, carbon free deposits of mullite can be obtained over a much broader range of input parameters compared to 1000 °C.

Effect of Pressure

Pressure was varied from 2 torr to 150 torr. The results are shown in the CVD phase diagrams in Figures 14. As the pressure is increased from 2 to 150 torr, the region over which mullite can be formed widens, and a fewer number of phases are present. Additionally, as the pressure is decreased from 150 to 2 torr, the level of free carbon is reduced (also compare these figures with Figure 10). Lower pressures are preferred for obtaining carbon-free deposits, since at lower pressures, carbon has a higher affinity to form gaseous products such as CH_4 than forming a solid deposit. Thus there is a trade-off between the extent of formation of mullite and obtaining carbon-free deposits.

Effect of Stoichiometry

To determine the appropriate ratios of the Al and Si species in the reactant mix, AlCl_3 and SiCl_4 concentrations were varied at the 1000 °C and 75 torr condition. The region over which the compositions were varied is shown on the ternary diagram with the lines AA, BB and CC in Figure 15. CO_2 concentration throughout the line AA was maintained at 90 moles. Thus, the total ($\text{AlCl}_3 + \text{SiCl}_4$) concentration was 10 moles. AlCl_3 composition was varied from 0 to 10 moles, and the results were plotted in terms

of composition of the reaction products and the AlCl_3 deposition efficiency. The deposition efficiency is calculated by dividing the number of moles of the product by the number of moles of AlCl_3 that contributes to that product. Figure 16 shows the concentration and efficiency curves. Mullite concentration was found to increase gradually with increasing AlCl_3 concentration with the highest at 7.5 moles of AlCl_3 , which also matches with the stoichiometry of mullite. The SiO_2 concentration in the deposit is the highest at 0 moles of AlCl_3 and reduces to zero at 7.5 moles AlCl_3 . Al_2O_3 concentration increases from zero at 7.5 moles AlCl_3 to its highest at 10 moles of AlCl_3 . The efficiency of mullite formation is 100 % from 0 to 7.5 moles of AlCl_3 , at which point Al_2O_3 starts to form.

Section BB was taken at the constant CO_2 concentration line of 50 moles as shown in Figure 15, thus the total $\text{AlCl}_3 + \text{SiCl}_4$ concentration is 50 moles. AlCl_3 concentration was varied from 0 to 50 moles (SiCl_4 from 50 to 0 moles). The results of the calculations were plotted in terms of AlCl_3 concentration. Figure 17 shows the concentration and efficiency profiles. The trends observed in this case were very similar to the ones in the previous case, except that the efficiency of mullite formation is the highest when the Al:Si ratio is that of stoichiometric mullite. In addition, carbon was observed as a product throughout the analysis.

Section CC was taken at a constant SiCl_4 concentration of 3 moles. Thus, the total ($\text{AlCl}_3 + \text{CO}_2$) concentration was 97 moles. AlCl_3 concentration was varied from 10 to 80 moles (87 to 17 moles of CO_2). Figure 18 shows the concentration and efficiency diagrams. The concentration of the resulting mullite remains fairly constant throughout the diagram. However, the efficiency of mullite formation is the highest at the low AlCl_3 concentration. It is evident from the phase diagram that it is important to operate in the

mullite+Al₂O₃ region is now smaller than before. The SiC+SiO₂+C region is approximately the same size as when AlCl₃ and SiCl₄ were used. SiC+SiO₂ region is now much larger, and SiO₂+C region starts to appear at lower CO₂ concentrations than before; however, the overall region is smaller than before.

When AlCl₃ and SiCl₄ were replaced with AlF₃ and SiF₄, a completely different phase diagram emerges. A halide phase AlF₃ is observed at low CO₂ concentrations and high AlF₃ concentrations. This indicates that at low oxygen concentrations, AlF₃ does not react with the available hydrogen in order to form HF and Al as a deposit. A large region of pure Al₂O₃ is also observed in the diagram. Mullite is mostly observed along the SiF₄-CO₂ line, and is again seen as a line compound, but formed over a much narrower range of reactant concentrations. In addition, there was a region near the high CO₂ concentration where no solid phases were formed.

This confirms that using the AlBr₃ and SiBr₄ and AlF₃ and SiF₃ systems does not provide any added benefit, and that in fact they are not favorable for producing mullite through this method. Thus only the SiCl₄ and AlCl₃ combination was used for experimentation.

Mullite Deposition

Reactant concentrations in the deposition experiments were varied within the general ranges investigated in the thermodynamic analysis. Deposition of α -Al₂O₃ via hydrolysis of AlCl₃ was used as a guideline in establishing the initial process characteristics such as the reactor geometry (fixturing, sample holders). However, it was

later found that the optimum reactor geometry necessary for mullite deposition was entirely different from that for alumina. Reactants were introduced from the bottom of the chamber and exhausted from the top. Si_3N_4 and SiC substrates were placed at three different levels within the constant temperature hot-zone. A block diagram representing the process is as shown in Figure 21. AlCl_3 was formed by chlorinating the Al chips like in the case of Al_2O_3 deposition. SiCl_4 was evaporated from liquid stage at room temperature.

Deposition was generally non-uniform along the length of the reactor. This is due to the fact that the system consisted of a hot wall reactor, and the reactants are depleted as they pass through the reactor via deposition on the fixtures and the reactor walls. However, the deposition was uniform in the radial direction, and the coatings were fairly uniform within the length of the 20 mm long samples, except for the approximately 1-2 mm portion of the substrate that was held in the fixture. Growth rates were calculated by dividing the total weight gain in a sample by the total surface area, thus making it convenient for comparison. For a typical experiment at 950 °C and 75 torr condition for 120 minutes, the samples gained an average weight of 5 mg, thus making the growth rate approximately 0.0138 $\text{mg}/\text{cm}^2\text{-min}$. The $\text{AlCl}_3\text{:SiCl}_4$ ratio in the input reactant mixture was 2:1. A comparison of the experimental and calculated equilibrium rates and efficiencies indicates that for each specific set of conditions, the experimental deposition rates and efficiencies were less than the theoretical rates and efficiencies. This means that generally, thermodynamic equilibrium conditions were not attained in the conditions studied in this reactor geometry.

The coating starts with very fine grains and grows into larger grains as the growth process continues. It can also be seen that the grains grow in a columnar fashion thus supporting the fact that there is an orientation effect within the coating.

Although all the electron diffraction patterns in the TEM taken at various points within the coating confirmed that the coating was mullite, several variations in grain structure were observed. Figure 26 shows a cross-section TEM micrograph of a typical mullite coating on SiC. An initial nano-crystalline layer was observed (as confirmed by fringes in electron diffraction), and then large crystals of columnar mullite, often starting with small equiaxed crystals. A detailed TEM and STEM analysis was presented elsewhere. [31] Chemical analysis on the STEM indicated that in addition to the microstructural variations, there is also a pronounced compositional variation through the thickness of the coating. Al/Si ratio varied from as low as 1.5 at the substrate/coating interface to as high as 8 near the surface. Al/Si composition increased gradually through the nanocrystalline region, and then at the interface with the crystalline region, a sharp jump in Al/Si ratio was observed. The composition of the coating was found to be uniform parallel to the coating/substrate interface throughout the coating. Thus, the compositional variation is not random, and is only in the growth direction. This effect was investigated through variations in temperature, pressure, reactant gas stoichiometry, and the coating evolution with time.

Effect of Temperature

Temperature was varied between 800 °C and 1050 °C at 50 °C increments. All the experiments were carried out at a constant pressure of 75 torr, keeping all the reactant

stoichiometries constant. The corresponding SEM coating surface micrographs, EDS spectra, and X-ray diffraction patterns are shown in Figures 27 to 29. The coating deposited at 800 °C has a very globular morphology as opposed to a faceted morphology at 950 °C. X-ray diffraction indicates that there is no detectable crystalline phase present in the coating. Nevertheless, Al and Si were both present in the coating as shown by the EDS spectrum. The Al/Si ratio was approximately 2:1. At 850 °C the coating has a predominantly globular structure with small faceted crystals growing from the large grains. X-ray diffraction indicates a small detectable amount of mullite in the coating. To my knowledge this is the lowest temperature ever at which crystalline mullite was reported synthesized by any process. Although it is hard to estimate, it would be safe to say that the coating has no specific orientation at this stage. The Al/Si ratio in the EDS analysis was 2.65. At 900 °C, the globular grains are smaller, and the crystallites start to grow. In addition, a network of cracks was observed, indicating that there may be stresses between the amorphous and the crystalline "layers" of the coating possibly due to thermal mismatch upon cooling, or during growth. X-ray diffraction analysis shows mullite as the only crystalline phase present in the coating. The diffraction pattern indicates that there is no specific orientation in the deposit. EDS analysis indicates the Al/Si ratio near the surface as 3.77. At 1000 °C, much larger grains compared to the 950 °C case were observed. In addition, large clusters of crystals were also observed, usually accompanied by a network of microcracks around them. These cracks could be due to the growth stresses resulting from growth mismatch between the coating and the large clusters. Thus, higher temperatures promote deposition and hence grain growth. X-ray diffraction analysis indicates that the coating was oriented just the same way as the coating at 950 °C. The Al/Si ratio near the surface was calculated to be 4.56. At 1050 °C, very large crystals were observed. These crystals appear to grow by "dominating" the small crystals underneath. Again, X-ray diffraction indicates that the coatings were

highly oriented. Temperatures above 1050 °C could not be attained with the current system, although the furnace was capable of temperatures up to 1200 °C, due to problems with efficiently maintaining the reactor base temperature below the allowable operating temperature of the Viton® o-ring.

The effect of temperature on the deposition rate is shown in Figure 30. The mullite deposition rate decreased from 800°C to 850°C and then increased. Figure 31 shows the Arrhenius plot corresponding to an activation energy 7.4 kcal/mol. Although this activation energy is characteristic of a mass-transport limited process, the result should be interpreted with caution since a variation in Al/Si ratio was observed in the coating. In addition, the extent of crystallinity was also a variable.

Effect of Pressure

Pressure was varied between 50 and 200 torr, keeping the temperature constant at 950 °C. The corresponding SEM micrographs, EDS spectra, and X-ray diffraction analyses are presented in Figures 32 - 34. At 50 torr, relatively small crystallites were formed compared to the 75 torr condition. The growth rates were also lower. At the 100 torr condition, grains with varying sizes were observed on the surface. At the 150 torr condition, a much larger grain size was observed, again with a range of grain sizes within the coating. X-ray diffraction analysis indicates that the grains are not as oriented as in the 75 torr condition. Also the Al/Si ratio as observed by the EDS analysis is lower than that at the 75 torr case. At 200 torr, the coating is not very dense, and exhibits major porosity through large spaces left between crystals. The crystals appear to be growing independent of the surface beneath them, unlike in the previous cases, where the crystals were growing at the expense of other grains. It is as if these crystals were nucleating

irrespective of the chemistry of the surface beneath them. The Al/Si ratio was high at 5.75. The growth rate, and thus the grain size, however, were lower than in the 150 torr condition, a reversal in the trend with pressure observed so far. This is possibly because the reaction starts to slow down as the total pressure is increased beyond a certain level, although further experimentation is required to fully understand this reaction. Pressures in the order of 300 torr and above could not be attained because of limitations such as condensation of the AlCl_3 vapor in the feed-through at the base of the reactor due to the increased residence time. A simple calculation shows that the residence time at 300 torr would be 1 second in the hot zone, four times the amount observed at 75 torr.

The effect of total system pressure on deposition rate is shown in Figure 35. The deposition rate increased almost linearly at low system pressures; however, with a further increase in system pressure, the rate of increase was reduced, with a subsequent reduction in the deposition rate. This effect can be attributed to the depletion of reactants with increase in pressure due to the hot wall deposition system.

Effect of Stoichiometry

The AlCl_3 and SiCl_4 concentrations were varied keeping the rest of the reactants and the deposition conditions constant. This set of experiments were carried out at the 950 °C and 75 torr condition. The corresponding SEM micrographs, X-ray diffraction patterns, and the EDS analyses are presented in Figures 36 - 38. When only SiCl_4 was introduced, globular grains of approximately 5 μm size were observed. X-ray diffraction analyses indicate no detectable crystalline phase in the coating. When the AlCl_3 : SiCl_4 ratio was maintained at 1:2, a large difference in grain size was observed. The grains were much smaller, in the order of 1 μm , with an occasional crystallite within the coating. When the AlCl_3 : SiCl_4 ratio was increased to 2:3, a very interesting morphology was

Comparison of the growth rates at various levels in the reactor and the reactant depletion effects suggest that the formation of mullite does not require the formation of H_2O through the water-gas-shift reaction. Further experimentation is necessary in order to understand the exact mechanism involved.

Coating Evolution

To understand the nucleation and growth characteristics of mullite on Si_3N_4 and SiC , a number of experiments were carried out at the 950°C and 75 torr condition. Coatings were grown for varied amounts of time in order to estimate the growth rates and morphologies with respect to time. Because in-situ observations cannot be made in this hot wall reactor, separate experiments had to be carried out for 30, 60, 90, 120, and 150 minutes. The corresponding SEM micrographs, EDS spectra, and X-ray diffraction analyses of the samples processed for different times are presented in Figures 40 - 42. After 30 minutes of deposition, the coating appears to have a globular morphology with some large grains dominating the growth process. The EDS spectra show that the Al:Si atomic ratio in the coating was 1.12. The coating is very uniform and is approximately $1\ \mu\text{m}$ thick. After 60 minutes, fine crystals start to form on top of the globular grains. The Al: Si ratio as seen from the EDS analysis is 2.91. At this stage, the coating is approximately $2.5\ \mu\text{m}$ thick. After 90 minutes, the coating appears to be completely crystalline with the grains growing much larger. The Al: Si ratio in the coating is 4.54. The coating is now approximately $5\ \mu\text{m}$ thick. The 120 minute condition was discussed earlier. After 150 minutes, the grains continue to grow to approximately $10\ \mu\text{m}$ size. The Al: Si ratio is now at a high 7.35. The coating is now approximately $15\ \mu\text{m}$ thick. There seems to be a rapid increase in coating growth rate as time progresses. This also further confirms that the Al content in the mullite coating is proportional to the growth rate.

Based on the observations, it can be inferred that the mullite coating in general starts being low in Al content, irrespective of the inlet gas composition. The coating grows at a relatively slow pace with a gradual increase in Al content. At a certain stage when a critical Al concentration is reached in the deposit, crystallites start to nucleate and then grow into large crystals in a columnar fashion. The growth rate and the Al content increase with time. One possible explanation for this is that since the coatings are grown on SiC and Si₃N₄, Si may have a natural tendency to nucleate faster than Al. Pure SiO₂ produced by the hydrolysis of SiCl₄ is amorphous. This is possibly the reason why the coatings start off being "amorphous". The slow nucleation of Al in turn could cause a build-up of Al species at the reacting surface. Since the difference between the bulk gas concentration of Al and surface concentration of Al is now lower. This is not completely understood and further experimentation is required. Thus, the Al species in the bulk gas stream will end up reacting with the H₂O in the "gas phase", resulting in powder formation. This is supported by the fact that initially (lower deposition times) the Al content in the powders collected was high. However, experiments with long times (120 minutes) yielded powders with low Al content. Thus, once Al starts to nucleate on the surface at a faster rate, the concentration gradient across the boundary layer is steep, causing the Al flux to increase. In addition, the orientation of mullite crystals in the c-axis direction and the increase in Al content points out to the fact that there is preferential nucleation and growth of Al, once the crystallite is formed. In essence, from a CVD process perspective, for Al nucleation, initially the rate-limiting step appears to be nucleation, and then possibly diffusion through the boundary layer.

Solid Solubility Range of Mullite

Crystalline mullite was detected by X-ray diffraction when the Al:Si atomic ratio in the coating estimated by EDS spectra was as low as 1:1. This result could be misleading since EDS analysis gives an overall composition of the coating, whereas X-ray diffraction analysis reveals only the crystalline phases present in the coating. Thus, it is difficult to estimate the lower limit for the composition of mullite through this method, especially since any excess SiO_2 present in the coating is most likely in an amorphous form, and would not be detected by X-ray analysis. On the other hand, at the upper limit, the Al:Si atomic ratios calculated from the EDS spectra can be used as an exact indication of the composition of mullite, since the coating is in crystalline form, at least to appearance, and also since no Al_2O_3 peaks were detected by X-ray diffraction. With this assumption, the highest Al:Si atomic ratio observed in the coatings was at the condition when the experiment was run for 150 minutes, and is 7.35. This translates to an $\text{Al}_2\text{O}_3:\text{SiO}_2$ ratio of 3.685. This was the highest observed at this set of process conditions. This does not mean that this is the highest attainable Al stoichiometry in mullite via CVD or by any other method for that matter. Based on the trends in the experiments at this stage, longer times would probably yield mullite coatings with higher Al content.

Powder Synthesis

At high concentrations of the chlorides, (AlCl_3 and SiCl_4), considerable amount of powder was formed in the chamber. Very low concentration of chlorides resulted in

runs with little powder in the chamber, but also with low growth rates. In general at higher pressures more powder was observed. The powders made appeared to be crystalline in nature as confirmed by X-ray diffraction. Figure 43 shows the X-ray diffraction pattern of a typical mullite powder. The "hump" at the lower 2θ angles indicates that there may be a certain amount of amorphous phase present in the powder. The powders, however had varying compositions all the way from very Al rich to very Si rich based on the process conditions. Figure 44 shows the SEM and TEM micrographs of the powders. The TEM micrograph of a single grain shows that there is an orientation effect even in powders. In addition, they are probably oriented along the c-axis growth direction.

Adhesion Testing

Adhesion is possibly the most important characteristic of a coating to be considered irrespective of the environment in which it will be used. Coating/substrate adhesion is mainly dependent on the atomic interactions between the coating and the substrate material. Extent of diffusion between the substrate and the coating to a large extent defines the adhesion strength of the coating/substrate combination. CVD being a thermal process aides the necessary solid-state diffusion to enable sharing of atoms/molecules between the coating and the substrate. In addition, there are often chemical interactions between the substrate material and the reacting gases resulting in intermediate compounds, further enhancing the adhesion. Factors such as a mismatch in thermal expansion coefficient, coating porosity, and substrate preparation may also affect adhesion to a great extent. In case of mullite on SiC and Si₃N₄, as discussed earlier, CTE mismatch does not appear to be a major factor. In addition, the coatings were, in general,

of 9 $\mu\text{m}/\text{sec}$. All scratches were made from the substrate into the coating. Figures 46 and 47 show the scratch tracks on SiC and Si_3N_4 samples mounted in cross-section. No failure in the form of delamination of the coating was observed in mullite coatings on SiC. This is attributed to the match in thermal coefficient of expansion between mullite and SiC, thus minimizing the stresses upon cooling. Unlike the case of the macro-scratch test, the substrate material does not really have an impact on the critical load via the failure of the substrate underneath the coating. Thus, the critical load for mullite on SiC is estimated to be higher than 100 g. Loads in excess of 100 g were not possible due to limitations with the diamond indenter. In case of Si_3N_4 , cracks were observed right at the coating/substrate interface, indicating delamination at a critical load of 100 g.

Corrosion Testing

Corrosion resistance evaluation was performed at Oak Ridge National Laboratory. Mullite coated Si_3N_4 samples were exposed to $\text{Na}_2\text{SO}_4+\text{O}_2$ atmosphere for 100 hours at 1000 °C. Initial results from the analysis look very promising. [32] Figure 48 shows a back-scattered electron image along with X-ray elemental maps of the mullite coating in cross section after hot corrosion. The dot maps show that the coating is intact at both the $\text{Na}_2\text{SO}_4/\text{mullite}$ and $\text{mullite}/\text{Si}_3\text{N}_4$ interfaces, and that no diffusion of Na_2SO_4 through the coating was observed. A small amount of Na was present at the Na_2SO_4 interface. In comparison, a Si_3N_4 sample tested at identical conditions reacted significantly with Na present to depths in the order of 20 mm. In addition, X-ray diffraction analyses performed before and after hot corrosion show that no additional phases were formed, and that the coating was stable, and retained its crystalline structure as shown in Figure 49. The natural tendency of the mullite coatings to increase in Al content as the

deposition progresses may have helped in the superior corrosion resistance of these coatings, since it was believed that a high Al mullite, or an Al_2O_3 +mullite composite would perform better than stoichiometric mullite under hot corrosion environments.

SUMMARY AND CONCLUSIONS

Three different routes to grow CVD mullite coatings have been investigated. Multi-layers of CVD SiO_2 and $\alpha\text{-Al}_2\text{O}_3$ coatings were grown on Si_3N_4 and SiC substrates. Heat treatment of these coatings resulted in cracking and delamination at the $\text{SiO}_2/\text{Al}_2\text{O}_3$ interface prior to the diffusion formation of mullite. It was determined that this failure was due to transformations within the TEOS grown vitreous SiO_2 layer, and that the phase transformations were primarily due to stresses created at the $\text{SiO}_2/\text{Al}_2\text{O}_3$ interface due to thermal expansion mismatch.

Thermodynamic analysis of the $\text{TEOS-AlCl}_3\text{-CO}_2\text{-H}_2$ mixtures showed that under equilibrium conditions, mullite can be formed for certain process parameters. Although the coatings had Al:Si ratios at the stoichiometric level, and the process could be altered to grow coatings with varying Al/Si ratios, the process essentially resulted in amorphous coatings. This was not pursued further since amorphous coatings are not suitable for high temperature applications with operating temperatures in the order of the transformation temperature of the coating due to difficulties similar to the ones encountered in the multi-layered route.

Equilibrium thermodynamic analysis was performed on the $\text{AlCl}_3\text{-SiCl}_4\text{-CO}_2\text{-H}_2$ system in order to evaluate the formation of mullite. CVD ternary phase diagrams were constructed for process variations between AlCl_3 , SiCl_4 and CO_2 . Concentration and deposition efficiency plots were also calculated for certain conditions. It was found that

pure mullite can be obtained at high CO₂ concentrations. In addition, the CVD phase plots show that low concentrations of the chlorides need to be used in order to obtain high deposition efficiency, and carbon-free deposits. It was also found that there was no underlying benefit to using bromides and fluorides as alternative halide sources. The information from the phase diagrams was effectively used as a guideline in identifying the initial process conditions for experimentation.

A CVD reactor was constructed for the direct deposition of mullite. Mullite coatings were grown for the first time via CVD. Certain process conditions also yielded crystalline mullite powders. Adherent and dense mullite coatings were grown on Si₃N₄ and SiC substrates. The only crystalline phase found by X-ray diffraction analysis was mullite. It was found that mullite coatings can only be grown within a fairly narrow window of experimental conditions. The coating evolution with time was investigated. The coating in general started off with a high Si amorphous phase, and increased in Al concentration. At a certain critical Al concentration, crystallites started to form and with time grew into large crystals. The crystals grew in the c-axis direction and oriented themselves in the [001] direction. The size of the crystals increased with time to a certain point and then reduced due to the rapid growth rate. Totally amorphous, partly crystalline, and completely crystalline surfaces were obtained based on the process parameters. Increasing temperature in general yielded larger crystals and thicker coatings. Higher pressures resulted in larger crystallites, but resulted in porous coatings due to the high growth rates and low area coverage. Increase in Al content in the inlet gas mixture resulted in larger crystal size and higher Al content on the surface.

The coatings in general exhibited superior adhesion characteristics. Adherence of mullite coatings on SiC substrates was better than that on Si₃N₄ substrates. A typical

critical load in macro-scratch test was above 100 N, and in micro-scratch test was 100 g on Si_3N_4 and exceeded that on SiC. The coatings performed very well under Na_2SO_4 salt and O_2 atmospheres at 1000 °C for 100 hours. The superior corrosion characteristics of these coatings could be attributed to the natural tendency of the coatings to increase in Al content, resulting in graded coatings.

Further studies are required in order to optimize these coatings. There currently exists inadequate information concerning the kinetics, nucleation, and growth of mullite on Si-based substrates. This information is necessary to develop a useful corrosion resistant coating for high temperature applications.

Figure 1 Various Reaction Paths to Obtain Mullite Coatings

Figure 2 Schematic Representation of the CVD System

Figure 3 SEM Micrograph of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ Multi-layered coating with Al and Si Line Scans

Figure 4 X-Ray Diffraction Pattern of the Multi-layered coating after anneal at 1200 °C

Figure 5 TEM Micrograph of Al_2O_3 - SiO_2 Interface After Annealing at 1200°C for 2 hours

Figure 6 a) TEM Micrograph of Al₂O₃-SiO₂ Interface showing delamination of the Multi-layered coating annealed at 1350 °C for 2 hours showing (inset) the diffraction pattern of the crystalline SiO₂ layer, b) Schematic of the Coating Configuration

T=1270 °C ; Time = 2hr

*{101} Peak of α -Cristobalite

Figure 7 Effect of Pressure on Devitrification of SiO₂ Powders

Figure 8 CVD Phase Plots of the $\text{TEOS-AlCl}_3\text{-CO}_2\text{-H}_2$ System at a) 800 °C and 50 Torr, b) 800 °C and 100 Torr, c) 900 °C and 50 Torr, d) 1000 °C and 50 Torr (Contd.....)

Figure 9 EDS Analysis of Codeposited Coatings With a) Low Si Content, b) Medium Si Content, c) High Si Content

Temperature	1000 °C
Pressure	75 torr
H ₂ : (AlCl ₃ +SiCl ₄ +CO ₂)	5:1
H ₂ Concentration	500 moles

Figure 10. CVD Ternary Phase Diagram of AlCl₃-SiCl₄-CO₂-H₂ System at 1000 °C and 75 Torr

Figure 11 CVD Binary Phase Diagram of AlCl_3 - SiCl_4 - CO_2 - H_2 System at 1000°C and 75 Torr

Figure 12 CVD Ternary Phase Diagrams of $AlCl_3$ - $SiCl_4$ - CO_2 - H_2 System at a) 800 °C, and b) 1200 °C, both at 75 Torr

Figure 13. CVD Ternary Phase Diagram of AlCl_3 - SiCl_4 - CO_2 - H_2 System at 1000 °C and 75 Torr

Temperature
1000 °C
Pressure
75 torr
$\text{H}_2:(\text{AlCl}_3+\text{SiCl}_4+\text{CO}_2)$
5:1
H_2 Concentration
500 moles

Figure 14 CVD Ternary Phase Diagram of $\text{AlCl}_3\text{-SiCl}_4\text{-CO}_2\text{-H}_2$ System at 1000 °C and a) 2 Torr, and b) 150 Torr

Figure 15 CVD Ternary Phase Diagram of AlCl₃-SiCl₄-CO₂-H₂ System at 1000 °C and 75 Torr

Figure 16 a) Concentration, and b) Efficiency Curves at Section AA in Figure 15

Figure 17 a) Concentration, and b) Efficiency Curves at Section BB in Figure 15

Figure 18 a) Concentration, and b) Efficiency Curves at Section CC in Figure 15

Figure 19 CVD Ternary Phase Diagram of AlCl₃-SiCl₄-CO₂-H₂ System at 1000 °C and 75 Torr; H₂ Concentration: a) 1000 Moles, b) 250 Moles

Figure 20 CVD Ternary Phase Diagram of a) $AlBr_3$ - $SiBr_4$ - CO_2 - H_2 System, and b) AlF_3 - SiF_4 - CO_2 - H_2 System at 1000 °C and 75 Torr

Number	Temperature	Pressure	Reactant Mixture
	° C	torr	
1.	1000	75	AlCl ₃ -SiCl ₄ -CO ₂ -H ₂
2.	1000	2	
3.	1000	25	
4.	1000	150	
5.	800	2	
6.	800	25	
7.	800	75	
8.	800	150	
9.	1200	2	
10.	1200	25	
11.	1200	75	
12.	1200	150	
13.	1000	75	H ₂ : 1000 moles
14.	1000	75	H ₂ : 250 moles
15.	1000	75	AlBr ₃ -SiBr ₄ -CO ₂ -H ₂
16.	1000	75	AlF ₃ -SiF ₄ -CO ₂ -H ₂

Table 1 Deposition Conditions Used in the Thermodynamic Analysis of the AlCl₃-SiCl₄-CO₂-H₂ System

Figure 21 Schematic Representation of the CVD Mullite Deposition Process

Figure 22 SEM Micrograph of Mullite Coating on Si_3N_4 at 950 °C and 75 Torr, a) Surface, and b) Fractured Cross-Section

Figure 23 X-Ray Diffraction Pattern of Mullite Coating Deposited on Si₃N₄ at 950 °C and 75 Torr

Figure 24 X-Ray Diffraction Pattern of Stoichiometric Mullite Powder

Figure 25 a) TEM Cross-Section Micrograph of Mullite Coating on Si_3N_4 , and b) Electron Diffraction Pattern of Mullite Coating

Figure 26 TEM Cross-Section Micrograph of Mullite Coating on SiC Showing Details of the Nanocrystalline and Columnar Regions

Figure 27 SEM Micrograph of Mullite Coating Deposited on Si_3N_4 at 75 Torr and a) 800 °C, b) 850 °C, c) 900 °C, d) 950 °C, e) 1000 °C, and f) 1050 °C

Figure 27 SEM Micrograph of Mullite Coating Deposited on Si_3N_4 at 75 Torr and a) 800 °C, b) 850 °C, c) 900 °C, d) 950 °C, e) 1000 °C, and f) 1050 °C (Contd.....)

Figure 27 SEM Micrograph of Mullite Coating Deposited on Si_3N_4 at 75 Torr and a) 800 °C, b) 850 °C, c) 900 °C, d) 950 °C, e) 1000 °C, and f) 1050 °C (Contd.....)

Figure 28 X-Ray Diffraction Pattern of Mullite Coating on Si₃N₄ at 75 Torr and a) 850 °C, b) 900 °C, and c) 1000 °C

Figure 29 EDS Analysis of Mullite Coating on Si_3N_4 at 75 Torr and a) 800 °C, b) 850 °C, c) 900 °C, and d) 1000 °C; The Unidentified Peak is Conductive Au Coating on the Sample

Figure 30: Effect of process temperature on mullite deposition rate at 75 torr.

Figure 31: Arrhenius plot of mullite deposition at 75 torr.

Figure 32 SEM Micrograph of Mullite Coating Deposited on Si_3N_4 at 950 °C and a) 50 Torr, b) 100 Torr, c) 150 Torr, and d) 200 Torr

Figure 32 SEM Micrograph of Mullite Coating Deposited on Si_3N_4 at 950 °C and a) 50 Torr, b) 100 Torr, c) 150 Torr, and d) 200 Torr (Contd.....)

Figure 33 X-Ray Diffraction Pattern of Mullite Coating on Si_3N_4 at 950 °C and a) 50 Torr, and b) 200 Torr

Figure 34 EDS Analysis of Mullite Coating on Si_3N_4 at 950 °C and a) 50 Torr, and b) 200 Torr; The Unidentified Peak is Conductive Au Coating on the Sample

Figure 35: Effect of total system pressure on mullite deposition rate at 950°C.

Figure 36 SEM Micrograph of Mullite Coating Deposited on Si_3N_4 at 950 °C and 75 Torr; Al:Si Ratio in the Input Gas Composition a) 0:1, b) 1:2, c) 2:3, d) 1:1, e) 3:1, and f) 4:1

Figure 36 SEM Micrograph of Mullite Coating Deposited on Si_3N_4 at 950 °C and 75 Torr; Al:Si Ratio in the Input Gas Composition a) 0:1, b) 1:2, c) 2:3, d) 1:1, e) 3:1, and f) 4:1 (Contd.....)

Figure 36 SEM Micrograph of Mullite Coating Deposited on Si_3N_4 at 950 °C and 75 Torr; Al:Si Ratio in the Input Gas Composition a) 0:1, b) 1:2, c) 2:3, d) 1:1, e) 3:1, and f) 4:1 (Contd.....)

Figure 36 SEM Micrograph of Mullite Coating Deposited on Si_3N_4 at 950 °C and 75 Torr; Al:Si Ratio in the Input Gas Composition a) 0:1, b) 1:2, c) 2:3, d) 1:1, e) 3:1, and f) 4:1 (Contd.....)

Figure 37. X-Ray Diffraction Pattern of Mullite Coating on Si_3N_4 at 950 °C and 75 Torr; Al/Si Ratio in the Input Gas Composition: a) 1:2, b) 2:3, and c) 4:1

Figure 38 EDS Analysis of Mullite Coating on Si_3N_4 at 950 °C and 75 Torr; Al/Si Ratio in the Input Gas Composition: a) 1:2, b) 2:3 (Crystalline Region), c) 2:3 (Amorphous Region), d) 1:1, and e) 4:1; The Unidentified Peak is Conductive Au Coating on the Sample

Figure 38 EDS Analysis of Mullite Coating on Si_3N_4 at 950 °C and 75 Torr; Al/Si Ratio in the Input Gas Composition: a) 1:2, b) 2:3 (Crystalline Region), c) 2:3 (Amorphous Region), d) 1:1, and e) 4:1; The Unidentified Peak is Conductive Au Coating on the Sample (Contd.....)

Figure 39: Effect of Al/Si (input) ratio on mullite deposition rate at 950°C and 75 torr.

Figure 40 SEM Micrograph of Mullite Coating Deposited on Si_3N_4 at $950\text{ }^\circ\text{C}$ and 75 Torr; Deposition Time: a) 30 Minutes, b) 60 Minutes, c) 90 Minutes, and d) 150 Minutes

Figure 40 SEM Micrograph of Mullite Coating Deposited on Si_3N_4 at 950 °C and 75 Torr;
Deposition Time: a) 30 Minutes, b) 60 Minutes, c) 90 Minutes, and d) 150 Minutes
(Contd.....)

Figure 41 X-Ray Diffraction Pattern of Mullite Coating on Si_3N_4 at 950°C and 75 Torr ; Deposition Time: a) 60 Minutes, b) 90 Minutes, and c) 150 Minutes

Figure 42 EDS Analysis of Mullite Coating on Si_3N_4 at 950 °C and 75 Torr; Deposition Time: a) 30 Minutes, b) 60 Minutes, c) 90 Minutes, and d) 150 Minutes; The Unidentified Peak is Conductive Au Coating on the Sample

Figure 43 X-Ray Diffraction Pattern of CVD Mullite Powder; The "Hump" in the Lower 2 θ Angles Suggests that there is a Certain Amount of Amorphous Phase

Figure 44 a) SEM Micrograph, and b) TEM Micrograph of Mullite Powder Showing High Orientation Effect

Figure 45 Macro-Scratch Track of Mullite Coating on a) SiC Showing Failure, and b) Si_3N_4 Showing No Failure

Figure 46 Micro-Scratch Track of Mullite Coating on SiC Mounted in Cross-Section at
a) 50 g Load, and b) 100 g Load

Figure 47 Micro-Scratch Track of Mullite Coating on Si_3N_4 Mounted in Cross-Section at
a) 50 g Load, and b) 100 g Load

Figure 49 X-Ray Diffraction Analysis of Mullite Coating on Si_3N_4 After Hot Corrosion Showing No Phase Change Within the Coating or the Substrate

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