**Functionally Graded Alumina/Mullite Coatings for Protection
of Silicon Carbide Ceramic Components from Corrosion**

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EXECUTIVE SUMMARY

The main objective of this research project is the formulation of processes that can be used to prepare compositionally graded alumina/mullite coatings for protection from corrosion of silicon carbide components (monolithic or composite) used or proposed to be used in coal utilization systems (e.g., combustion chamber liners, heat exchanger tubes, particulate removal filters, and turbine components) and other energy-related applications. Mullite will be employed as the inner (base) layer and the composition of the film will be continuously changed to a layer of pure alumina, which will function as the actual protective coating of the component. Chemical vapor deposition reactions of silica, alumina, and aluminosilicates (mullite) through hydrolysis of aluminum and silicon chlorides in the presence of CO_2 and H_2 will be employed to deposit compositionally graded films of mullite and alumina. Our studies will include the kinetic investigation of the silica, alumina, and aluminosilicate deposition processes, characterization of the composition, microstructure, surface morphology, and mechanical behavior of the prepared films, and modelling of the various deposition processes.

During this reporting period, the construction and development of the chemical vapor deposition system was completed, and experiments were conducted on the deposition of alumina, silica, and aluminosilicates (such as mullite) from mixtures of AlCl_3 and CH_3SiCl_3 in CO_2 and H_2 . Work was mainly done on the investigation of the effects of the reaction temperature on the deposition kinetics. It was found that the temperature had a positive effect on the single oxides deposition rates and the codeposition rate. The apparent activation energy values extracted from the deposition rate vs. temperature curves in the high temperature region were similar for the three deposition processes, having a value around 20 kcal/mol. The codeposition rates were higher, by a more than a factor of 2 in some cases, than the sum of the deposition rates of the two oxides in the independent experiments at the same operating conditions, and this result led to the conclusion that there should exist additional surface reaction steps in the codeposition process, that lead to solid formation and involve both silicon-containing and aluminum-containing species. The elemental analysis (EDXA) of films deposited from $\text{MTS-AlCl}_3\text{-CO}_2\text{-H}_2$ mixtures showed that silicon oxide was the main component, and comparison of the deposition rates of SiO_2 and Al_2O_3 during codeposition with those seen in single species deposition experiments at the same conditions revealed that the codeposition process was characterized by a dramatic enhancement of the deposition of SiO_2 and an equally dramatic reduction in the rate of Al_2O_3 deposition. Since the enhanced codeposition rate was caused by increased silicon oxide deposition, it was concluded that the main deposition product of the additional surface reaction steps in codeposition must be silicon oxide. A comprehensive investigation of the effects of the other operating parameters on the kinetics of the codeposition process will be carried out in the next reporting period.

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1. BACKGROUND INFORMATION

Silicon-based ceramic materials are used or being considered for use in a variety of applications related to coal utilization and other energy-related systems. In particular, silicon carbide (SiC), in monolithic or composite form, exhibits such a unique combination of high thermal shock resistance, high thermal conductivity, high strength, low weight, and high oxidation resistance at elevated temperatures that it appears to be the material of choice for a number of technological applications. These include structural components in advanced coal technologies, such as IGCC (integrated gasification combine cycle) and PFBC (pressurized fluidized-combustion) systems, components of advanced turbine systems (combustor liners and, possibly, turbine blades), parts in piston engines (valves and piston heads), ceramic tubes as heat exchangers in coal-fired boilers and industrial furnaces (glass melting and aluminum remelt operations), and ceramic filters for particulate from hot flue and coal gases.

Like Si itself and other Si-based ceramics and intermetallics (silicon nitride and molybdenum disilicide, for instance), the good oxidation resistance of SiC at high temperatures is due to the formation of a scale of SiO_2 , through which the oxidizing agent (O_2) must diffuse to reach unreacted material. SiO_2 has one of the lowest diffusion coefficients of O_2 (Jacobson, 1993), and as a result, this passive oxidation process is a slow process. At very high temperatures, formation of gaseous SiO becomes possible, and the oxidation process moves into a phase of active oxidation, where because of absence of a protective scale, the rate of the reaction is very high (Wagner, 1958; Pareek and Shores, 1992; Zheng et al., 1992; Sickafoose and Readey, 1993; Nickel et al., 1993). This pattern of oxidation is qualitatively the same for all Si-based materials, but the location of the passive to active oxidation transition boundary on the [oxygen partial pressure, temperature] plane varies with each material (Jacobson, 1993).

In a typical application, there are several trace components present in the combustion environment in addition to fuel and oxygen. Among the most important ones are alkalis (Na, K), halides (Cl, I), and sulfur (S). All these pollutants are present in relatively large quantities in coal and other solid fuels (waste material, for instance), but even some of the cleanest fuels (such as, unleaded gasoline, commercial aviation fuel, and

fuel oils) contain significant amounts of sulfur (0.05-1%) and alkali compounds (4-20 ppm) (Jacobson, 1993). Sodium and halides may also be introduced in the combustion system through the combustion air, especially if combustion occurs in the vicinity of a marine environment. Corrosive degradation of ceramic components occurs by both gaseous and liquid species formed from the various alkali, halide, and sulfur precursors in the high-temperature environment.

Alkali-induced corrosion through liquid deposition of alkali metal salts and oxide slags is the major mechanism of corrosion. The main corrosive species is Na_2O (or K_2O), formed from sulfites or other salts, which tends to react with the protective scale of SiO_2 forming liquid sodium silicate species ($\text{Na}_2\text{O} \cdot (\text{SiO}_2)_x$). In contrast to SiO_2 , this liquid layer is not protective because the diffusion coefficient of oxygen in it is much higher than that in SiO_2 and because in the high temperature environment it is carried away from the surface through vaporization. The situation is exacerbated in the presence of moisture since more reactions that lead to formation of Na_2O become thermodynamically more favorable (Van Roode et al., 1993). This corrosion process is not much different from the hot corrosion of turbine alloys that is observed under Na_2SO_4 generating conditions and the corrosion that occurs in SiC heat exchanger tubes when alkali halide fluxes are used in the aluminum remelt industry. Surface recession rates of almost 1 cm/yr may be observed under these circumstances (Goldfarb, 1988; Van Roode et al., 1993).

Given the exceptional properties of SiC and of other silicon-based ceramics but their problematic performance in alkali and sulfur containing environments, a protective coating must be used on surfaces exposed to the combustion environment to protect them from corrosion. For proper performance, such a coating must have good oxidation resistance and chemical stability (up to at least 1300°C), good adherence with the base material, and good tolerance to thermal cycling. Problem-free performance during thermal cycling requires that the chosen material must be such that it yields low residual stress at the interface, and this in turn necessitates that there is a good match between the thermal expansion coefficient of the substrate and that of the coating.

Alumina presents very good corrosion resistance against the various corrosive compounds that cause degradation of the silica scale that functions as a protective layer of

Si-based ceramics (Goldfarb, 1988; Lawson et al., 1993). Under some conditions the presence of Na_2O in the sodium salt melts can lead to formation of a β/β' -alumina (Van Hoek et al., 1991,1992), but, as it is evidenced from the long-term, stable performance of β' -alumina ceramics as electrolytes in Na/S cells, further reaction between the β/β' -alumina and the sulfur and alkali compounds is practically absent (Gordon et al., 1992). Its high corrosion resistance combined with its relatively low cost makes alumina an ideal candidate as protective coating for silicon carbide, but the problem is that its thermal expansion coefficient is almost twice as large as that of the latter.

In such intractable problems such as joining dissimilar materials (metals and ceramics) and depositing adherent and crack-free films and coatings on substrates having significantly different thermal expansion coefficients, compositionally graded materials (CGM's) provide practical solutions (Ford and Stangle, 1993). In graded materials the composition is varied continuously or in steps between those of two outermost layers. The continuous change in the composition and, hence, microstructure of CGM's results in gradients in their properties, and this makes possible to develop coherent structures that present considerably different properties at the two ends of their thickness. Of particular interest for application to protective coatings is the ability of CGM's to bridge the difference in the thermal expansion coefficients of a base layer, which adheres well to the substrate and matches well its thermal expansion coefficient, and of an outer layer, which exhibits the desired properties of chemical stability and corrosion resistance. By spreading the mismatch of the thermal expansion coefficient over a finite thickness, the local thermal stresses – compressive or tensile depending on which thermal expansion coefficient is larger and in which direction the temperature is changed – are reduced and excessive damage to the coating is avoided (Ford and Stangle, 1993).

It is practically impossible to find a single material that matches the thermal expansion coefficient of the substrate material (SiC for our studies), adheres well to the substrate, and exhibits good oxidation resistance in the presence of alkali, sulfur, and halogen compounds. Good oxidation resistance more or less requires that the coating be an oxide, but going through a database of thermal expansion coefficients of oxide ceramics, one soon comes to the realization that there is no oxide that both has thermal

expansion coefficient matching that of SiC over the whole temperature range and provides acceptable protection against oxidation and corrosion. There is relatively good agreement between the thermal expansion coefficient of mullite and SiC, but, even though mullite does not contain free silica, there is some evidence in the literature that it tends to form sodium aluminosilicates and silicates in an alkali and sodium environment (Dietrichs and Krönert, 1982; Van Roode et al., 1993). As we mentioned in the previous section, much better corrosion resistance is displayed by alumina, but its thermal expansion coefficient is almost a factor of 2 greater than that of SiC. The above discussion points to the conclusion that a solution to the problem is offered by a compositionally graded structure, in which the composition varies smoothly between a base layer of mullite, used to provide good adhesion and matching of the thermal expansion coefficient, and an outer layer of alumina, which protects the substrate against corrosion and oxidation.

To reduce the mismatch between alumina and silicon carbide substrates, Federer et al. (1989) and Van Roode et al. (1993) produced graded coatings with composition varied in 25% steps between that of mullite (inner layer) and alumina (outer coating) using a plasma spraying method. Their corrosion tests showed that the mullite-alumina graded structures did very well during thermal cycling, showing no visible damage and developing only a few cracks. However, examination of the substrate-coating interface revealed the presence of sodium aluminosilicates ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) and, possibly, sodium silicates. Their conclusions were that the problem lied in the porosity (10-15%) of the coating produced by plasma spraying and that denser coatings were needed for successful application of the graded coating concept.

The development of processing routes for the fabrication of mullite/alumina graded ceramic coatings through chemical vapor deposition (CVD) methods is the subject of the present research proposal. Silica and alumina will be deposited using mixtures of their chlorides with H_2 and CO_2 , and the composition of the deposit will be varied normal to the surface by changing the temperature, pressure, or composition of the gas phase. Experimental deposition studies will be carried out in a hot-wall reactor coupled with a thermogravimetric analysis system, which has already been used successfully in

our laboratory to study SiC deposition from methyltrichlorosilane. Detailed kinetic models of the deposition processes of silica, alumina and mullite will be developed along the general lines of the procedures we used to do so for SiC deposition. These models will be used for data analysis and process scale-up. The deposits will be characterized by a variety of methods (XRD, Raman spectroscopy, electron microscopy, EDX, and electron microprobe analysis) and will be tested for corrosion using various procedures.

2. WORK DONE AND DISCUSSION

During the six months of this reporting period, the construction and development of the chemical vapor deposition system was completed, and experiments were conducted on the chemical vapor deposition of alumina, silica, and aluminosilicates from mixtures of AlCl_3 and methyltrichlorosilane (CH_3SiCl_3 , MTS) in H_2 and CO_2 . The experimental study of this deposition system in this reporting period was mainly concentrated on the investigation of the effects of the reaction temperature on the deposition kinetics. The experimental apparatus and the experimental procedures used in carrying out chemical vapor deposition experiments are described in the following section, and the presentation and the discussion of some of the obtained results are given next.

2.1. Description of the CVD Apparatus

A schematic flow diagram of the CVD apparatus is shown in Figure 1. The deposition source gases are MTS, CO_2 , and H_2 for the case of silica deposition, AlCl_3 , CO_2 , and H_2 for alumina deposition, and MTS, AlCl_3 , CO_2 , and H_2 for codeposition. Aluminum trichloride is formed *in situ* in a packed-bed reactor (chlorinator), loaded with high purity aluminum granules (99.9% purity). A hydrogen-hydrogen chloride mixture is supplied in the chlorinator, and AlCl_3 is produced through the reaction:

The chlorinator is heated with a flexible electric heating tape, and its temperature is maintained above 250°C since it has been reported that at such temperatures the conversion of HCl to AlCl_3 is complete (Fredriksson and Carlsson, 1993). This result was verified by analyzing the effluent of the chlorinator.

The deposition experiments were carried out in a vertical hot-wall reactor with 15 mm id, made of quartz. A stream of hydrogen (purge gas) is sent continuously to the reactor through the housing of the microbalance (Figure 1), its role being to prevent the corrosive reactants (MTS and AlCl_3) and corrosive products formed in the reactor (HCl and other Cl-containing compounds) from entering the housing and destroying the weighing mechanism. The purge gas is mixed with the $\text{AlCl}_3\text{-H}_2$ stream, which enters the reactor tube through a small side tube at about 18 cm from the top of the heating zone of the furnace. MTS (99.97 % purity) is supplied to the reactor through a second side tube, by sending through a bubbler containing liquid MTS a metered stream of carrier gas (hydrogen) and using a carrier-based mass flow control system to monitor and control its delivery rate. Carbon dioxide is sent to the reactor through the same side tube after it is mixed with MTS. Of course, in the case of alumina deposition only the stream of CO_2 enters the reactor through this side tube.

The pressure in the deposition chamber is measured at the inlet of the CVD reactor using a capacitance manometer, and it is regulated by a throttling valve controlled by a pressure controller. Subambient pressures are generated using a mechanical vacuum pump, and the pump and the valve are protected by using a liquid nitrogen trap to condense the gaseous reactants and products exiting the reactor, a soda lime trap to remove HCl vapors that escape from the liquid nitrogen trap, and a particulate filter to remove solid particles formed in the reactor or entrained from the solid trap.

The deposition rate is monitored by employing an electronic microbalance (Cahn D-101). The substrate used for deposition is hung from the sample arm of the microbalance with a very thin refractory wire inside the chemical reactor. Its weight is recorded continuously as a function of time, and rates of deposition are obtained by differentiating the weight vs. time curve. The reactor tube and the substrate are heated with a high temperature single-zone resistance furnace, which provides 23 cm of heating zone. Two Pt/Pt-Rh (S-type) thermocouples are placed in proximity to the reactor at the center of the heating zone to record the chamber temperature. The reading of one of these two thermocouples is used to control the temperature of the reactor, while the role of the second one is to enable the controller to shut down the furnace in case of thermal

runaway. The side tube through which MTS and CO₂ are introduced in the reactor is located at 36 cm from the top of the heating zone of the furnace, and this provides sufficient time for the mixing of the source gases with the H₂ purge stream. Temperature measurements in the reactor showed that the part of the reactor tube that lies in the heating zone is almost isothermal.

The procedure of the conducted experiments consisted of evacuating the reactor, introducing the H₂ stream, setting the reactor to the operating pressure and temperature, and sending the carrier gas through the bubbler. The reverse procedure was employed at the end of each experiment. The deposition of silica, alumina, and aluminosilicates took place on SiC substrates suspended with thin molybdenum wire in the reactor tube within the isothermal zone. The substrates had 1.35 cm length, 0.75 cm width, and 0.20 mm thickness, and they were obtained by depositing SiC from mixtures of methyltrichlorosilane and hydrogen on substrates made out of high density graphite. It should be noted that the signal of the microbalance, before the introduction of the reactant mixture, was employed to examine whether significant leakage of oxygen into the reactor took place. At the high temperature used in the experiments, the reaction of oxygen with the graphite substrate is fast, and therefore, a significant amount of oxygen leaking into the reactor would cause the weight of the substrate to decrease. The original material had 7-10% open porosity with an average pore size of ~2000 Å, and thus, in order to prevent the deposition measurements from being corrupted by deposition occurring within the pores, silicon carbide was deposited at a high temperature (1000°C) on the substrate until a constant rate of weight variation with time was obtained. At each set of experimental conditions, the deposition process was allowed to occur for a period of time that was sufficient to extract a reliable deposition rate from the slope of the weight vs. time curve.

2.2. Presentation and Discussion of the Results of Deposition Experiments

Results on the effect of temperature on the deposition rate are presented in Figure 2 in Arrhenius-plot coordinates, that is, as $\ln R_d$ vs. $1/T$, with R_d being the deposition rate and T the absolute temperature in the reactor. To obtain these results, the temperature was varied between 800 and 1100°C at 25°C increments. The mole fractions of the source

gases were 0.011 MTS (x_{MTS}), 0.009 AlCl_3 (x_{AlCl_3}), and 0.036 CO_2 (x_{CO_2}). The midpoint of the substrate was located 7 cm from the top of the heating zone of the furnace, the total flow rate was $250 \text{ cm}^3/\text{min}$, and the operating pressure 100 Torr. The choice of the employed Al/Si feed ratio (0.8) was based on the results of preliminary experiments, which showed that comparable deposition rates of the two single oxides (Al_2O_3 and SiO_2) could be obtained in independent deposition experiments for similar values of mole fractions of the source gases (AlCl_3 and MTS). At this stage of our investigation, our objective was to investigate the feasibility of depositing aluminosilicate species, and therefore, it was decided to operate under conditions giving similar rates of Al_2O_3 and SiO_2 deposition. Deposition rate vs. temperature data are presented in Figure 2 for both the codeposition and the independent single species deposition experiments at the same chloride and CO_2 concentrations.

For all three cases, it is seen that the rate increases with increasing temperature. In the case of silica deposition, the rate varies in the range $0.002\text{-}0.05 \text{ mg/cm}^2\cdot\text{min}$ for temperatures between 925 and 1100°C . Our experiments showed that the deposition of silica proceeds at a very low rate (lower than $10^{-3} \text{ mg/cm}^2\cdot\text{min}$) for temperatures below 925°C . This observation is in agreement with the thermodynamic analysis of the Si/C/Cl/H/O system and the results we presented in the previous report if it is assumed that SiCl_2 is the main deposition precursor. The decomposition of MTS is thermodynamically favored throughout the entire range of temperatures examined, but SiCl_2 becomes the dominant silicon-chlorine species above 1200 K ($\sim 925^\circ\text{C}$). The apparent activation energy of the reaction of silica formation, the slope of the $\ln R_d$ vs. $1/T$ curve, is calculated by employing linear regression, and is found to be 25.92 kcal/mol . There is not any information available in the literature on the deposition of silica from MTS so as to compare this value with other reported activation energies. Only some work on silica deposition through hydrolysis of SiCl_4 has been done during the last few years in the context of preparation of selectively permeable membranes for hydrogen separation (Tsapatsis et al., 1991, Tsapatsis and Gavalas, 1992) and atomic layer controlled growth of SiO_2 on silicon surfaces (Sneh et al., 1995; Klaus et al., 1997).

In the case of alumina deposition, two temperature regions can be distinguished in the behavior of the reaction rate vs. temperature plot shown in Figure 2, corresponding to different slopes of the curve. Above 950°C, the rate of increase of the alumina deposition rate with temperature (slope of the curve in Arrhenius coordinates) is markedly higher than in the second region that lies between 800 and 950°C. This difference can be attributed to the fact that at low temperatures, the water gas-shift reaction is very slow. In their experiments, Choi et al. (1987) showed that the nucleation and growth of Al_2O_3 are closely related to the production of H_2O which was found to be exponentially increased as the temperature was rising. However, the Al_2O_3 CVD does not exclusively depend on the water formation in the gas phase since the activation energy for the homogeneous water formation reaction (78 kcal/mol at temperatures from 800 to 1000°C (Fredriksson and Carlsson, 1993)) is higher than the reported activation energies of alumina deposition. Calculated activation energies in past experimental studies vary from 15.5 to 56.7 kcal/mol (Iida and Tsujide, 1972; Funk et al., 1976; Silvestri et al., 1978; Colmet and Naslain, 1982; Colmet et al., 1982; Kim et al., 1982; Park et al., 1983). The experimental data of Figure 2 yield an activation energy of 19.6 kcal/mol for temperatures higher than 950°C. The differences in the activation energies obtained in different studies is not surprising considering that in almost all cases they correspond not to the true activation energy of the reaction, but they are apparent quantities that also account for the effects of the reactor geometry, flow and temperature field in the reactor, and residence time. Moreover, the overall deposition process is not represented by a single elementary irreversible reaction, which is the only case where the activation energy can be extracted from the $\ln R_d$ vs. $1/T$ plot.

The deposition rate of Al_2O_3 over the examined temperature range (800-1100°C) varies from 0.002 to approximately 0.05 $\text{mg}/\text{cm}^2\cdot\text{min}$ (Figure 2). Temperatures higher than 950°C should be employed in order to obtain relatively high deposition rates of alumina. This is consistent with the thermodynamic analysis of the equilibrium gas phase of the Al/C/Cl/H/O system if AlCl and AlCl_2 exhibit higher surface reactivities and, hence, higher Al_2O_3 deposition rates than AlCl_3 (see previous report). Significant reduction of the equilibrium mole fraction of AlCl_3 was observed only at temperatures

above 1200 K, which implies that alumina deposition is favored throughout this temperature region. Most past studies on the deposition of alumina from mixtures of AlCl_3 , CO_2 , and H_2 employed temperatures higher than 900°C . Kim et al. (1982) and Park et al. (1983) obtained results at experimental conditions similar to those used in this study (100 Torr, 0.005-0.01 AlCl_3 mole fraction, 0.005-0.03 CO_2 mole fraction). The reported values of deposition rate are in good agreement with our results for temperatures above 1000°C , but they obtained higher deposition rates at lower temperatures. The actual precursors of deposition are not the gaseous species fed into the chemical reactor but rather the products of their decomposition reactions, and the concentrations of the latter at the deposition location are influenced strongly not only by the operating conditions but also by the characteristics of the chemical reactor, the flow field in it, and the residence time. Thus, the differences between the results of this study and those of Kim et al. (1982) and Park et al. (1983) are not surprising since, for instance, the flow rate in the latter was twice the value used here. Similar remarks generally apply to the differences among the results of other deposition studies.

Funk et al. (1976), Colmet and Naslain (1982) and Colmet et al. (1982) also reported a sharp increase of the alumina deposition rate with the substrate temperature above 950°C . In the experiments of those studies, the total pressure was 50 Torr, and the total gas flow rate 560, 300, and $300\text{ cm}^3/\text{min}$, respectively. Their results are comparable with our observations even though their CVD system was operated at much lower pressure and the characteristics of their reactors were different. They found apparent activation energies larger than the values obtained here (40, 31.2 and 31.2 kcal/mol , respectively). A high apparent activation energy (76.5 kcal/mol) was also calculated by Bae et al. (1998) at an operating pressure of 100 Torr. This is the only reported value that is very close to the activation energy of the water formation from CO_2 and H_2 , and suggests that the water gas-shift reaction may be the rate-limiting step of Al_2O_3 deposition.

The temperature also has a strong effect on the rate of the codeposition process (Figure 2). The codeposition rate varies within the range $0.001\text{-}0.2\text{ mg/cm}^2\cdot\text{min}$, (a range of two orders of magnitude), for temperatures between 800 and 1100°C . Higher

codeposition rates are observed for the codeposition process than for each of the single oxides in independent deposition experiments, with the only exception being at 800°C where the rate of alumina deposition is larger. The codeposition rates are not only larger than those of the single oxides but also higher than their sum by a factor of 2-3 (composite curve in Figure 2). This is a surprising result considering that the concentration of each of the chlorides in the codeposition process was the same as that in the corresponding single species deposition experiments. This was also the case for the concentration of CO₂ and the concentration of H₂, because of the very low chloride mole fractions.

The results of Figure 2 indicate that in the codeposition process there must be additional surface reaction steps leading to solid formation, that involve both silicon-containing and aluminum-containing species. Since the codeposition rate is much higher than the sum of the deposition rates of the single oxides at the same conditions, the rates of these surface reactions must be much larger than those of the surface reactions that lead to deposition of single oxides in the independent experiments. The latter must also be present in the codeposition system. It must be noted that since continuous monitoring of the deposition rate was employed in our experiments, it was possible to measure the rates of the codeposition process and the two single species deposition processes sequentially at each set of experimental conditions. Therefore, the differences seen among the deposition rates of the three processes in Figure 2 and in other figures reflect the differences in the gas phase composition and not in other operating conditions. Figure 3 presents the variation of the weight of the substrate with time in the three deposition processes, as they were performed sequentially at 1000°C at the conditions of Figure 2.

From a comparison of the individual deposition reactions in Figure 2, it is found that for temperatures up to 925-950°C the deposition of alumina proceeds at higher rate than that of silica, whereas at higher temperatures the opposite situation prevails. If the relative rates of SiO₂ and Al₂O₃ deposition in the codeposition process were proportional to those seen in the single species deposition experiments at the same conditions, one would expect the deposit to contain significant quantities of Al₂O₃ at all temperatures and its composition to be biased towards this oxide in the low temperature range. However,

the analysis of the composition of the codeposited films, using energy dispersive X-ray analysis (EDXA), revealed that SiO_2 was the main constituent, with its content exceeding in many cases 95% (on weight basis). Table I shows results of the composition of the films at various combinations of operating conditions along with the rates measured for the codeposition and the single oxide deposition processes, and the deposition rates for the SiO_2 and Al_2O_3 components of the codeposited films that were extracted from the values of the codeposition rate and film composition. Superscript *ind* is used to denote results from individual (single oxide) deposition experiments, and superscript *cod* to denote the respective quantities for codeposition experiments. It is seen that whereas the deposition rates from individual experiments predict SiO_2 content in the range 35 to 58%, the content of the codeposited film in this oxide is above 88% in all cases.

The high silicon oxide content of the deposit is, as the results of Table I indicate, the combined effect of a dramatic enhancement in the rate of silica deposition and a decrease in the rate of alumina deposition. The decrease in the rate of alumina deposition can be explained on the basis of the results of thermodynamic analysis. As it was pointed out in our previous report, the concentrations of aluminum-containing radical species in the equilibrated gas phase when AlCl_3 and MTS coexist in the feed are much lower, for comparable CO_2 and H_2 concentrations, than those when AlCl_3 is the only chloride fed into the system, whereas the concentration of HCl is much higher and comparable to that in the $\text{MTS-CO}_2\text{-H}_2$ system. Since the aluminum-containing radical species must be, because of their higher sticking coefficient, the principal precursors of alumina deposition, and HCl is the product of almost every Al_2O_3 deposition reaction step that one may construct, the rate of the deposition of Al_2O_3 in the codeposition process should be much lower if the gas phase composition in the reactor behaves as that of the equilibrated gas phase. However, the thermodynamic equilibrium results cannot explain the enhancement in the rate of SiO_2 deposition since the concentrations of the silicon-containing species in the codeposition process were found to be similar to (and in some cases lower than) those in the $\text{MTS-CO}_2\text{-H}_2$ system. It was pointed out above that the fact that the codeposition rate is greater than the composite deposition rate (sum of deposition rates of the two oxides) in independent experiments suggests that there must

be steps in the chemistry of the codeposition process that involve both aluminum- and silicon-containing species. Since the enhanced codeposition rate is caused by increased silicon oxide deposition, one is led to conclude that the main deposition product of those additional steps must be silicon oxide.

The activation energy that corresponds to the Arrhenius-plot of the codeposition process (Figure 2) is 22.90 kcal/mol, a value that lies between the activation energies of the individual deposition processes, and is three times bigger than the activation energy reported for codeposition from SiCl_4 , AlCl_3 , CO_2 , and H_2 (7.4 kcal/mol) by Mulpuri (1996). In the latter, deposition of mullite was carried out at conditions similar to those used here: temperatures in the range 800-1050°C, and 75 Torr pressure. It was reported that mullite did not form at 800°C, and that its deposition rate increased with temperature for temperatures higher than 850°C. The reported deposition rates are about one order of magnitude smaller than those found in this study, but this difference can be due to the different reactor configurations and deposition conditions and, more importantly, to the use of silicon tetrachloride as silicon source. It must be noted out that increasing deposition rate as a function of time, followed by an increase in the aluminum content of the deposit was observed by Mulpuri in his studies (1996). This observation is at variance with what we found in our studies, where the deposition rate was constant even when the deposition process was allowed to take place at fixed conditions for a few hours. Figure 4 shows the variation of the weight of the substrate with time at 950°C and 100 Torr. Clearly, no noticeable variation in the slope of the curve – the dashed curve gives the straight line obtained through linear regression – is observed over the whole time horizon of the experiment.

3. SUMMARY

The construction and development of the chemical vapor deposition system was completed, and experiments were conducted on the deposition of alumina, silica, and aluminosilicates (such as mullite) from mixtures of AlCl_3 and CH_3SiCl_3 in CO_2 and H_2 . The experiments in this reporting period were mainly concentrated on the investigation of the effects of the reaction temperature on the deposition kinetics. It was found that the

temperature had a positive effect on the single oxides deposition rates and the codeposition rate. The apparent activation energy values extracted from the deposition rate vs. temperature curves in the high temperature region were similar for the three deposition processes, having a value of about 20 kcal/mol.

The codeposition rates were higher, by a more than a factor of 2 in some cases, than the sum of the deposition rates of the two oxides in the independent experiments at the same operating conditions, and this result led to the conclusion that there should exist additional surface reaction steps in the codeposition process, leading to solid formation, that involve both silicon-containing and aluminum-containing species. The elemental analysis (EDXA) of films deposited from MTS-AlCl₃-CO₂-H₂ mixtures showed that silicon oxide was their main component, and comparison of the deposition rates of SiO₂ and Al₂O₃ during codeposition with those seen in single species deposition experiments at the same conditions led to the conclusion that the codeposition process was characterized by a dramatic enhancement of the deposition of SiO₂ and an equally dramatic reduction in the rate of Al₂O₃ deposition. Since the enhanced codeposition rate was caused by increased silicon oxide deposition, it was concluded that the main deposition product of the codeposition surface reactions steps was silicon oxide.

BIBLIOGRAPHY

Bae, Y.W., Lee, W.Y., Besmann, T.M., Cavin, O.B., Watkins, T.R., J. Am. Ceram. Soc., 81 (7), 1945 (1998).

Dietrichs, P., Krönert, W., INTERCERAM·NR. 3, 223 (1982).

Choi, S.W., Kim, C., Kim, J.G., and Chun, J.S., J. Mat. Sci., 22 (3), 1051 (1987).

Colmet, R., and Naslain, R., Wear, 80, 221 (1982).

Colmet, R., Naslain, R., Hagenmuller, P., and Bernard, C., J. Electrochem. Soc., 129, 1367 (1982).

Ford, R.G., Stangle, G.C., Proc. 6th Conf. Cer. Matrix Comp., p. 795 (1993).

Federer, J.I., Van Roode, M., Price, J.R., Surface and Coatings Technology, 39/40, 71 (1989).

- Fredriksson, E., and Carlsson, J.-O., J. Chem. Vap. Dep., 1, 333 (1993).
- Funk, R., Schachner, H., Triquet, C., Kornmann, M., and Lux, B., J. Electrochem. Soc., 123 (2), 285 (1976).
- Goldfarb, V., GRI Contract No. 5086-232-1274, Final Report (1988).
- Gordon, R.S., Heavens, S.N., Virkar, A.V., Weber, N., Corrosion Science, 33, 605 (1992).
- Iida, K., Tsujide, T., Jap. J. App. Phys., 11 (6), 840 (1972).
- Jacobson, N.S., J. Amer. Cer. Soc., 76, 3 (1993).
- Kim, J.G., Park, C.S., Chun, J.S., Thin Solid Films, 97 (1), 97 (1982).
- Klaus, J.W., Ott, A.W., Johnson, J.M., George, S.M., Appl. Phys. Lett., 70 (9), 1092 (1997).
- Lawson, M.G., Pettit, F.S., Blachere, J.R., J. Mater. Res., 8, 1964 (1993).
- Mulpuri, R., Chemical Vapor Deposition of Mullite Coatings on Silicon-based Ceramics for High Temperature Applications, Ph.D. Dissertation, Boston Univ. (1996).
- Nickel, K.G., Fu, Z., Quirnbach, P., Trans. ASME, 115, 76 (1993).
- Pareek, V.K., Shores, D.A., Science, 48, 983 (1992).
- Park, C.S., Kim, J.G., Chun, J.S., J. Vac. Sci. Technol. A, 1 (4), 1820 (1983).
- Sickafoose, R.R., Jr., Readey, D.W., J. Am. Cer. Soc., 76, 316 (1993).
- Silvestri, V.J., Osburn, C.M., Ormond, D.W., J. Electrochem. Soc., 125 (6), 902 (1978).
- Sneh, O., Wise, M.L., Ott, A.W., Okada, L.A., George, S.M., Surf. Sci., 334, 135 (1995).
- Tsapatsis, M., and Gavalas G. R., AIChE J., 38 (6), 847 (1992).
- Tsapatsis, M., Kim, S., Nam, S.W., Gavalas, G.R., Ind. Eng. Chem. Res., 30 (9), 2152 (1991).
- Van Hoek, J.A.M., van Loo, F.J.J., Metselaar, R., Key Eng. Materials, 53-55, 111 (1991).
- Van Hoek, J.A.M., van Loo, F.J.J., Metselaar, R., J. Am. Cer. Soc., 75, 109 (1992).

Van Roode, M., Price, J.R., Stala, C., J. Eng. Gas Turb. Power, 115, 139 (1993).

Wagner, C., J. Appl. Physics, 29, 1295 (1958).

Zheng, Z., Tressler, R.E., Spear, K.E., Corrosion Science, 33, 545 (1992).

**Table I. Composition analysis and rate data of codeposited films. R_d is measured in $\text{mg}/(\text{cm}^2 \cdot \text{min})$.
Operating pressure = 100 Torr; total flow rate = $250 \text{ cm}^3/\text{min}$; $x_{\text{MTS}} = 0.011$.**

$Pos. (cm)$	$T(^{\circ}C)$	X_{CO_2}	Al/Si (feed)	$(R_d)^{cod}$	$(wt\% SiO_2)^{cod}$	Al/Si (deposit)	$(R_d)_{SiO_2}^{ind}$	$(R_d)_{SiO_2}^{cod}$	$(R_d)_{Al_2O_3}^{ind}$	
4	1000	0.036	0.8	0.050	97.04	0.036	0.0137	0.0485	0.0135	0.0015
4	1000	0.072	2.5	0.165	88.27	0.16	0.0137	0.1456	0.0245	0.0194
7	1000	0.036	0.8	0.065	94.42	0.085	0.0157	0.0614	0.0160	0.0036
7	950	0.036	0.8	0.026	97.41	0.032	0.0047	0.0253	0.0057	0.0007

Figure 1. Schematic flow diagram of the chemical vapor deposition apparatus.

Figure 2. Deposition rate vs. temperature for the deposition and codeposition processes.

Figure 3. Variation of the weight of the substrate with time in the three deposition processes at 1000°C.

Figure 4. Variation of the weight of the substrate with time in the codeposition process at 950°C.