**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 six-month reporting period, we continued the work on the development and construction of the thermogravimetric chemical vapor deposition system that we intend to employ for studying the deposition of alumina, silica, and aluminosilicates (such as mullite) from mixtures of metal chlorides in H_2 and CO_2 . Specifically, we worked on the development of the tubular flow reactor that will be used for producing aluminum chloride for delivery to the chemical vapor deposition system and of the vapor and gas supply system. Various problems arising from condensation of aluminum chlorides in some sections of the supply line were resolved, and we expect to perform experiments using mixtures containing AlCl_3 in the next reporting period. Preliminary experiments on the deposition of SiO_2 from mixtures of methyltrichlorosilane (MTS) or tetrachlorosilane in H_2 and CO_2 were carried out, and the results showed that the deposition rates from MTS were much higher than those from SiCl_4 and comparable to those reported in the literature for alumina deposition from AlCl_3 - H_2 - CO_2 mixtures of similar composition. It was thus decided to employ MTS as silicon source in our codeposition experiments, and a comprehensive investigation of thermodynamic equilibrium in the Al/Si/Cl/C/O/H system for compositions corresponding to MTS- AlCl_3 - H_2 - CO_2 mixtures was conducted so as to identify the boundaries of the region of the space of operating parameters and conditions where preparation of functionally graded mullite/alumina coatings through CVD from metal chloride, CO_2 , and H_2 is feasible. The results showed that deposition of silica, alumina, mullite, and other aluminosilicates is feasible in a broad range of operating conditions from the equilibrated gas phase, but temperatures above 1148 K have to be employed to obtain deposits of alumina and mullite if the solid phases are also at equilibrium with each other.

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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 Na₂O 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, we worked on the construction of the tubular flow reactor (chlorinator) that will be used to deliver aluminum chloride to the chemical vapor deposition reactor, resolved a number of problems arising from condensation of aluminum chloride on the walls of the tubes that bring the aluminum chloride hydrogen mixture from the chlorinator to the chemical vapor deposition reactor. We expect to perform experiments using mixtures containing AlCl_3 in the next reporting period. Preliminary experiments on the deposition of SiO_2 from mixtures of methyltrichlorosilane (MTS) or tetrachlorosilane in H_2 and CO_2 were carried out, and the results showed that the deposition rates from MTS were much higher than those from SiCl_4 and comparable to those reported in the literature for alumina deposition from $\text{AlCl}_3\text{-H}_2\text{-CO}_2$ mixtures of similar composition. It was thus decided to employ MTS as silicon source in the codeposition experiments.

A comprehensive study of the thermochemical equilibrium of the Al/Si/Cl/C/O/H system for compositions corresponding to MTS, CO_2 , and H_2 mixtures was carried out in order to identify the boundaries of the region of the space of operating parameters and conditions where codeposition of alumina, silica, and aluminosilicates preparation of functionally graded mullite/alumina coatings through CVD from mixtures of metal chlorides, CO_2 , and H_2 is feasible. The results are presented and discussed in some detail below.

The mixture sent through the CVD reactor consists of H_2 , CO_2 , and AlCl_3 , and MTS, with the last two species supplied simultaneously only for codeposition experiments. Hydrogen and carbon dioxide react to produce water vapor through the

water gas-shift reaction, and deposition of silica, alumina, and aluminosilicates (e.g., $\text{Al}_6\text{Si}_2\text{O}_{13}$, and Al_2SiO_5) takes place through hydrolysis of MTS and AlCl_3 . The overall reactions that one may write to represent these processes are

The species fed into the chemical reactor undergo a number of decomposition and recombination reactions, before they reach the deposition surface, and thus, the actual chemistries of the deposition processes are much more complex than what the above overall reactions (equations (1)-(5)) suggest, involving several gas phase and solid phase (adsorbed on the deposition surface) species.

Results from the thermodynamic analysis of a reactive mixture used in a chemical vapor deposition process provide information that can be employed to determine the range of processing conditions where deposition of a particular solid species from that mixture becomes feasible, and identify from the large number of species that are typically present in the gas phase those that exist in significant quantities at equilibrium. The former of these findings is extremely helpful in selecting the operating conditions for the CVD process, whereas the latter can be used in deciding which of the gas phase species must be included in a mechanistic model for the chemistry of the process. Of course, since a CVD process is carried out at a finite residence time, while thermodynamic analysis assumes that infinite time is provided for the process, it is the heterogeneous and homogeneous chemistry of the process that determines whether deposition of a certain species can be obtained (e.g., see (Papasouliotis and Sotirchos, 1994) for SiC deposition). Moreover, the fact that a species does not exist in significant quantities in the equilibrium composition of the reactor does not necessarily imply that it is not important for its mechanism since it may participate in an important step of the kinetic pathway that leads to the deposition of the solid species of interest.

Thermodynamic equilibrium calculations were carried out on the Si/C/Cl/H/O, Al/C/Cl/H/O, and Al/Si/C/Cl/H/O systems using a computational scheme based on free energy minimization. The STANJAN code (Reynolds, 1986) was used for the computations, employing about 250 gaseous and condensed (solid) species with thermodynamic data taken from the JANAF Tables (Chase et al., 1985). Calculations were performed over broad range of operating conditions (temperature, pressure, and feed composition) for deposition of alumina, silica and aluminosilicates from mixtures of MTS, AlCl_3 , CO_2 , and H_2 . The temperature was varied in the range 800-1500 K, the cumulative mole fraction of the chlorides between 0.015 and 0.038, the CO_2 to chloride mole fraction ratio between 2 and 3, and the pressure between 20 and 760 Torr. The loading of the reactor in each element was determined from the feed composition in aluminum chloride, methyltrichlorosilane, hydrogen, and carbon dioxide.

The thermodynamic analysis was carried out in three steps: the free energy minimization code was first used to compute the equilibrium of the gas phase in the absence of solid deposition reactions. The composition of the equilibrated gas phase was subsequently employed to assess the feasibility of depositing a certain solid species by examining the equilibrium constants of reactions leading to the deposition of that species. Finally, the equilibrium constants of reactions among the solid species that were allowed to be deposited from the equilibrated gas phase, were used to determine transition temperatures for these reactions, and in this way determine the stability of the various solid species on the deposition surface. The justification behind following this three-step procedure is that the reactions that are encountered in the gas phase are, in general, much faster than those involved in solid deposition, and therefore, it is more likely within the residence times encountered in typical CVD reactors to have equilibration of the gas phase only. The attainment of complete gas-solid equilibrium requires that large amounts of mass be transferred from the gas phase to the solid phase, and this can happen only for unreasonably large residence times or deposition surface to volume ratios in the reactor.

The computations showed that 18 species were present at equilibrium in the reactor in significant quantities in the gas phase for the Al/Si/C/Cl/H/O system, 12 for the Si/C/Cl/H/O system, and 12 for the Al/C/Cl/H/O system, with the threshold mole fraction

taken as 10^{-6} . These species are shown in Table I. For the case of silica deposition (deposition from MTS), a representative variation of the equilibrium mole fractions of the major gas species with the temperature is shown in Figure 1 at 100 Torr. It is evident that almost complete decomposition of MTS takes place at equilibrium, especially at high temperatures. The radicals SiCl_3 and SiCl_2 are present in significant quantities, and since these species must exhibit high surface reactivity, this suggests that they may be main precursors for silicon incorporation in the deposit and, hence, silica deposition. Dichlorosilylene (SiCl_2) becomes the main silicon-bearing species above 1200 K. The role of SiCl_2 as the major silicon deposition precursor has been presented in experimental investigations of silicon deposition using silicon tetrachloride as source gas (Gupta et al., 1989; Aoyama et al., 1983).

It is seen in Figure 1 that silicon tetrachloride and SiHCl_3 are the two stable silicon chlorides that exist in appreciable quantities in the equilibrium gas phase composition. Because of their stable form these species are characterized by much lower surface reactivities than SiCl_2 and SiCl_3 , and therefore, their contribution to silicon incorporation in the deposit under conditions of gas phase equilibrium would be important only at low temperatures where their concentrations become much larger than those of SiCl_2 and SiCl_3 . A similar observation applies to CH_4 with regard to the role it plays, relative to other stable hydrocarbons and radicals, in carbon incorporation in the deposit (Papasouliotis and Sotirchos, 1994). This species is the only hydrocarbon that was found to exist above the mole fraction threshold (10^{-6}) in the equilibrated gas phase. Silicon monoxide (SiO) is the most abundant silicon-bearing species at temperatures above 950 K, its concentration becoming a few orders of magnitude larger than that of the next silicon-bearing species in the high temperature range. This result indicates that it would be necessary to include adsorption of this species on the surface in a mechanistic model of the process, but some studies have concluded that it possesses rather low surface reactivity (Walkup and Raider, 1988; Buss et al., 1992). Most of the chlorine is present in the form of HCl , one of the main products of the overall deposition reaction of SiO_2 from MTS and H_2O . Despite the high concentration of HCl , the deposition of SiO_2 from the equilibrated gas phase was determined to be feasible at all temperatures and all pressures

we investigated. However, if the formation of HCl occurs faster than the formation of H_2O , under actual deposition conditions, it is possible to have a situation in which the concentration of HCl in the gas phase would be at levels that have a strong inhibitory effect on the deposition process or lead to complete stoppage of deposition.

The temperature dependence of the equilibrium mole fractions of the major gas phase species involved in alumina deposition is shown in Figure 2 at the same pressure as in Figure 1. In contrast to the situation encountered in Figure 1, AlCl_3 is the main metal-bearing species at temperatures up to 1450 K. Significant amounts of other aluminum species, such as AlCl , AlCl_2 , and AlOH , appear above 1100 K, but because of their radical form, these species may possess high surface reactivities and, therefore, contribute more to the aluminum incorporation in the deposit. A much more interesting difference between the results of Figure 1 and Figure 2 is that in the latter the overall equilibrium concentration of the radical metal-containing species increases with the temperature and that the concentration of HCl at equilibrium is significantly lower. This difference suggests that the effects of temperature and HCl presence in the gas phase on the rates of the deposition of the single oxides may be markedly different. The deposition of alumina from the equilibrated gas phase of Figure 2 was found to be feasible at all temperatures, that is, any reaction leading to Al_2O_3 and involving species present in the gas phase had equilibrium constant greater than unity.

Results on the influence of temperature and initial concentration of the reacting mixture on the equilibrium composition of the gas phase for the case of the codeposition process are presented in Figures 3 and 4 at 100 Torr, with the metal chloride loadings in Figure 3 being the same as those in Figures 1 and 2. The comparison of Figure 3 with Figures 1 and 2 leads to a number of interesting observations. The addition of AlCl_3 in the mixture appears to influence weakly the concentration of the silicon species, but the converse is not true. Specifically, the introduction of MTS in the system leads to a dramatic reduction in the concentration of aluminum-containing radical species, such as AlCl , AlCl_2 , and AlOH . The concentration of HCl at all temperatures is similar to that in the $\text{MTS-H}_2\text{-CO}_2$ system, actually higher because of the introduction of additional chlorine in the system through AlCl_3 . By increasing the Al/Si feed ratio from 0.8 to 2.5

(Figure 4), a significant increase in the equilibrium mole fractions of the aluminum bearing radicals is observed, even in the low temperature region, and there is an appreciable decrease of the silicon species mole fractions, especially that of SiCl_2 . However, even in that, the concentration of HCl remains at levels similar to that in the $\text{MTS-H}_2\text{-CO}_2$ system, and the concentrations of the aluminum-containing radicals approach those seen in the absence of MTS only in the upper limit of the temperature range. It should be noted that because of the rise in the concentration of HCl , AlCl_2 becomes the most abundant aluminum-bearing species in the presence of MTS.

From the equilibrium constants of reactions leading to SiO_2 and Al_2O_3 deposition, such as Equations (2) and (3), it is concluded that the deposition of these two species is feasible at all temperatures in Figures 3 and 4, and the same conclusion was reached in other pressures. In view of the dramatic reduction in the concentration of aluminum-bearing radial species, and the increase in the concentration of HCl , this may be surprising for the case of Al_2O_3 , but as Figures 3 and 4 show, the concentration of AlCl_3 stays at very high levels. However, if AlCl_3 exhibits low surface reactivity and, therefore, low rate of Al incorporation in the deposit, the results of Figures 3 and 4 indicate that the decrease in the concentrations of AlCl , AlCl_2 , and AlOH and the concomitant increase in the concentration of HCl may influence strongly, in an adverse way, the rate of Al_2O_3 deposition.

The equilibrium constants of reactions (4) and (5) or other equivalent reactions show that the deposition of mixed oxides, Al_2SiO_5 and $\text{Al}_6\text{Si}_2\text{O}_{13}$, is also feasible at the conditions of Figures 3 and 4. From the thermodynamic data of the literature (Chase et al., 1985), it was determined that at the conditions chosen for our study, the most stable forms of these oxides are andalusite (Al_2SiO_5) and mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$). The formation of these mixed oxides from the single oxides can be represented by the reactions

Figure 5 presents the activity-based equilibrium constants of these reactions as functions of temperature. It is seen that the formation of the mixed oxides is feasible at all temperatures. The question that remains to be answered is what transformations, if any,

can take place among the single and mixed oxides and what are the transition (equilibrium) temperatures for these reactions. Two such reactions of interest for the deposition of mullite and their equilibrium temperatures are:

The variation of the equilibrium constant of these reactions is shown in Figure 5. Shown in this figure is also the equilibrium constant of the quartz (qrtz) to cristobalite (xbt) transformation,

as determined from thermodynamic data (Chase et al., 1985). From the above results it is concluded that: a) for $\text{Al}_2\text{O}_3:\text{SiO}_2$ ratio in the deposit below 1:1, the deposit will consist at equilibrium of Al_2SiO_5 and SiO_2 up to 1260 K, and $\text{Al}_6\text{Si}_2\text{O}_{13}$ and SiO_2 above that; b) for $\text{Al}_2\text{O}_3:\text{SiO}_2$ ratio between 1:1 and 3:2, it will consist of Al_2SiO_5 and Al_2O_3 up to 1128 K, Al_2SiO_5 and $\text{Al}_6\text{Si}_2\text{O}_{13}$ between 1128 and 1260 K, and $\text{Al}_6\text{Si}_2\text{O}_{13}$ and SiO_2 above 1260 K; and c) for $\text{Al}_2\text{O}_3:\text{SiO}_2$ ratio above 3:2, it will consist of Al_2SiO_5 and Al_2O_3 up to 1128 K, and $\text{Al}_6\text{Si}_2\text{O}_{13}$ and Al_2O_3 above that. In conclusion, if one is interested in the deposition of mullite, temperatures higher than 1128 K must be employed if there is thermodynamic equilibrium among the deposited solid species. The picture provided by the reactions represented by Equations (6)-(9) is relatively simple in comparison to that obtained through rigorous analysis of solid phase equilibrium in the Si/Al/O system, but it suffices for the purposes of our study since it provides results that are very close to those revealed by experimental and other thermodynamic studies. For instance, the estimated temperature of the “andalusite $\rightarrow$ mullite” transformation (1260 K) agrees well with the thermodynamic results of Davis and Pask (1971) who reported that at atmospheric and subambient pressures andalusite is the stable aluminosilicate species for temperatures lower than 1300 K, while near this temperature it transforms to mullite and silica quartz.

3. SUMMARY

During the six months of this reporting period, work was done on the construction of the gas and vapor delivery and reactor effluent treatment sections of the chemical vapor

deposition system and the thermodynamic analysis of chemical equilibrium of Al/Si/Cl/O/C/H systems having composition to that corresponding to mixtures of methyltrichlorosilane (CH_3SiCl_3 , MTS) and AlCl_3 in H_2 and CO_2 . It was decided to employ MTS as silicon source in our initial experiments because preliminary experiments showed that the rate of chemical vapor deposition of silica from mixtures of this species in H_2 and CO_2 is higher than that of mixtures of SiCl_4 of similar composition and comparable to the deposition rate of alumina from mixtures of AlCl_3 in H_2 and CO_2 .

The thermodynamic analysis results showed that deposition of silica alumina, mullite, and of other aluminosilicates from the equilibrated gas phase is feasible in a broad range of operating conditions. However, if chemical equilibrium exists among the various solid phases in the deposits, it is necessary to employ temperatures above 1148 K in order to obtain codeposits of alumina and mullite. When both chlorides (MTS and AlCl_3) are present in the gas phase, the concentrations of the aluminum chloride species (stable and radical) are much lower than those observed in the absence of MTS at the same AlCl_3 and CO_2 mole fraction, whereas the concentration of HCl is much higher. Since HCl is a product of most surface reaction steps leading to deposition of alumina, these results led us to conclude that if the aluminum chloride species are the main deposition precursors for aluminum incorporation in the deposit, the addition of MTS in the feed may lead to low rates of alumina deposition relative to those seen from mixtures of AlCl_3 , CO_2 , and H_2 .

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Table I. Major gas phase species of the thermodynamic analysis

CH_4	AlCl	SiCl_2
CO	AlCl_2	SiCl_3
CO_2	AlCl_3	SiCl_4
H_2	Al_2Cl_6	SiO
HCl	AlOH	SiHCl_3
H_2O	AlHO_2	SiH_2Cl_2

Figure 1. Equilibrium mole fraction vs. temperature for silica deposition at P=100 Torr. Solid phases were not allowed to form. $CO_2/MTS = 3.3$, $x_{MTS} = 0.011$.

Figure 2. Equilibrium mole fraction vs. temperature for alumina deposition at P=100 Torr. Solid phases were not allowed to form. $CO_2/AlCl_3 = 4$, $x_{AlCl_3} = 0.009$.

Figure 3. Equilibrium mole fraction vs. temperature for codeposition at $P=100$ Torr. Solid phases were not allowed to form. $CO_2/AlCl_3/MTS = 3.3/0.8/1$, $x_{MTS} = 0.011$.

Figure 4. Equilibrium mole fraction vs. temperature for codeposition at $P=100$ Torr. Solid phases were not allowed to form. $CO_2/AlCl_3/MTS = 6.6/2.5/1$, $x_{MTS} = 0.011$.

Figure 5. Equilibrium constant vs. temperature.