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TITLE: Compositionally Graded Alumina/Mullite Coatings for Protection of Silicon Carbide Ceramic Components from Corrosion

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I. ABSTRACT

OBJECTIVE: The main objective of this research project is the formulation of processes that can be used to prepare functionally 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.

WORK DONE AND CONCLUSIONS: The hot-wall, chemical vapor deposition reactor that was developed in the past under this project was used to complete the comprehensive investigation of the kinetics of the chemical vapor deposition of silica, alumina, and aluminosilicates from mixtures of aluminum chloride, silicon tetrachloride, CO_2, and H_2. In order to obtain results on the profiles of deposition rate and deposit stoichiometry along the length of the reactor from a single experiment, we used as substrates not only small graphite plates but also thin refractory wires traversing the axis of the reactor. Deposition experiments were also conducted using methyltrichlorosilane (MTS) as silicon source. In order to elucidate the effects of the coexistence of the two metal chlorides in the gas phase on the codeposition process, the kinetics of the deposition of the simple oxides were investigated as well. When MTS was used as silicon source, much higher deposition rates were observed, and the enhancement in the rate of codeposition, in comparison to the sum of the

deposition rates of the simple oxides, was more dramatic. As in the case of $SiCl_4$, this enhancement was chiefly due to an increase in the rate of silica incorporation in the deposit. The results for the deposition rate and deposit stoichiometry profiles indicated that it is possible to control the composition of the deposit through manipulation of the residence time of the mixture in the reactor.

SIGNIFICANCE TO THE FOSSIL ENERGY PROGRAM: Silicon carbide, in monolithic or composite form, exhibits such a unique combination of exceptional high temperature properties that it is ideally suited for use as structural component material in advanced coal technologies, such as IGCC (integrated gasification combined cycle) and PFBC (pressurized fluidized-combustion) systems. However, in the presence of alkali, sulfur, and halide species, SiC exhibits rather poor resistance to oxidation because the SiO_2 protective scale that is formed on its surface in an oxidizing environment is destroyed. Successful conclusion of this project will lead to development of methods that can be employed to prepare mechanically and thermally stable coatings for silicon carbide components that will be capable of undergoing a large number of thermal cycles without damage. It will also lead to preparation of protective coating for other materials with very good properties for energy-related applications, such carbon matrix composites.

PLANS FOR THE COMING YEAR: A mathematical model for silica, alumina, and aluminosilicate (mullite) deposition will be developed, and the model will be employed to analyze the experimental data. A detailed model for silica deposition has already been developed, and preliminary computations have shown it to be capable of predicting most patterns of behavior observed in the experiments including that of higher deposition rates from MTS.

II. HIGHLIGHT ACCOMPLISHMENTS

A chemical vapor deposition system was developed for preparation of metal oxide and other ceramic films through chemical vapor deposition.

The system was used to study the deposition of silica, alumina, and aluminosilicates from mixtures of $AlCl_3$ and $SiCl_4$ or CH_3SiCl_3 in H_2 and CO_2. The deposition reactions of the simple oxides (alumina and silica) were also investigated.

Comprehensive investigations of the thermodynamics aspects of the above deposition processes were carried out.

A detailed homogeneous and heterogeneous chemistry mathematical model for silica deposition was formulated, and preliminary work has been done on the modelling of alumina and aluminosilicate deposition.

III. OTHER INFORMATION

STUDENTS SUPPORTED BY THE GRANT: Igor M. Kostjuhin, Ph.D.
Stephanos F. Nitodas, Ph.D.

ARTICLES AND PRESENTATIONS:

Sotirchos, S.V., Kostjuhin, I., Hysteresis Phenomena in the Codeposition of SiC and C from Chlorosilane-Ethylene Mixtures, ACerS Annual Meeting, Cincinnati, OH, May 1997.

Sotirchos, S.V., Kostjuhin, I., Enhanced Deposition of Carbon from C2H4-H2 Mixtures in the Presence of Chlorosilanes, Proc. of the 14th Int. Conf. on CVD, pp. 512-519, The Electrochem. Soc., Pennington, NJ, 1997 (presented at the conference, Paris, September 1997).

Sotirchos, S.V., Kostjuhin, I., Chlorosilane Effects on the Preparation of Functionally Graded SiC/C Materials through CVD from Chlorosilane-Hydrocarbon-Hydrogen Mixtures, Annual MRS Meeting, Boston, December 1997.

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Nitodas, S.F., Sotirchos, S.V., Chemical Vapor Deposition of Alumina, Silica, and Aluminosilicates from Mixtures of Metal Chlorides, CO_2, and H_2, AIChE Annual Meeting, Miami, FL, November 1998.

Nitodas, S.F., Sotirchos, S.V., Kinetic Investigation of the Deposition of Alumina and Aluminosilicates from mixtures of $SiCl_4$, $AlCl_3$, CO_2, and H_2, to appear in MRS Proceedings, 1999 (presented at the MRS Annual Meeting, Boston, December 1998).

Nitodas, S.F., Sotirchos, S.V., Chemical Vapor Deposition of Aluminosilicates from Mixtures of $SiCl_4$, $AlCl_3$, CO_2, and H_2, submitted for publication.

Nitodas, S.F., Sotirchos, S.V., Codeposition of Silica, Alumina, and Aluminosilicates from Mixtures of CH_3SiCl_3, $AlCl_3$, CO_2, and H_2. Thermodynamic Analysis and Kinetic Investigation, submitted for publication.