ADMINISTRATIVE INFORMATION

1. **Project Name:** Advanced Composite Coatings for Industries of the Future

2. **Lead Organization:** PNNL
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3. **Principal Investigator:** Dr. Chuck Henager, Jr.
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4. **Project Partners:** **1)** University of Washington, Prof. Raj Bordia, 206-685-8158.
2) University of Central Florida, Prof. Lucille Giannuzzi 407-718-7708.
3) Air Products Research, Dr. Eric Minford, 610-481-3248.
4) Solar Turbines, Dr. Jeff Price, 619-544-5538.
5) SRI, Inc., Dr. Yigal Blum, 650-859-4367

5. **Date Project Initiated:** Project Initiated 10/1/2001 (FY-02), Current FY-04

6. **Expected Completion Date:** 9/30/06, FY-06.

PROJECT RATIONALE AND STRATEGY

7. **Project Objective:**

The proposed project will develop low-cost, ceramic coatings for prevention of high-temperature corrosion of metals and ceramics in industries such as chemical processing and industrial power generation. These coatings are targeted at providing high temperature (700-1000˚C) protection from corrosion due to oxidation, carburization, coking, and metal dusting.

8. **Technical Barrier(s) Being Addressed:**

Corrosion is an issue affecting many of the Industries of the Future and it is estimated to cost US industries $300 billion per year. Although corrosion resistant coatings are currently in use, enhanced performance requires improved coating materials and coating methods. Cost-effective coatings can save money by increasing the lifetime of industrial components and by allowing for the substitution of expensive materials by less-expensive substrate and coating combinations. In particular, a corrosion-resistant coating on 316-stainless steel would allow this material to be used in place of more expensive Ni-based or FeAl-based alloys where coking and/or metal dusting occurs. The main technical barrier is developing a low cost coating that survives repeated thermal cycling on 316-stainless steel.

9. **Project Pathway:**

To mitigate high temperature corrosion, two novel methods will be used to synthesize and fabricate ceramic-composite coatings suitable for large-scale field application: pyrolysis of preceramic precursors and in-situ displacement reaction synthesis. Non-oxide ceramic materials derived from inorganic, preceramic polymers have been found to possess exceptional high-temperature stability and oxidation resistance. Low-temperature processing and the ability to create tailored microstructures make this an attractive coating route. Composite coatings, containing several functional phases, provide an effective means for improving performance since compositions and microstructures can be tailored to address critical problems. Coatings produced by these methods are expected to be tough and corrosion resistance, with superior mechanical properties (wear, spallation resistance, etc.) compared to conventional coatings. The goal is to develop coatings so that the technology can be transferred to industrial customers or coating suppliers. The program will be a partnership that includes raw materials suppliers, coatings suppliers, industrial end-users, university researchers, and Pacific Northwest National Laboratory.

10. **Critical Technical Metrics:**

<u>Baseline Metrics</u>

- Corrosion is an issue affecting many of OIT's Industries of the Future and it is estimated to cost US industries $300 billion per year. Although corrosion resistant coatings are currently in use, enhanced performance requires improved coating materials and coating methods.
- 316SS is not used for steam-methane reformer piping since it is prone to metal dusting so a more expensive alloy is used instead, such as an Inconel alloy. The proper coating on 316SS would allow it to be used at 800-900˚C in a steam-reformer for several years.
- Aluminizing coatings can be applied to steels to form a protective coating but this process is expensive and environmentally unfriendly.

<u>Project Metrics</u>

- An inexpensive, environmentally friendly coating that can be applied to a high-expansion metal, such as 316S or 310SS will be developed.
- The coating must be initially adherent and survive at least 10 thermal cycles to 800˚C. It must also survive 1000 hrs at 800˚C in initial testing in air.
- Coatings must be tested for 1000 hrs in a lab-scale steam-reformer environment where flowing gas at 800˚C is used.
- Coating cost and ease of application are paramount. Ideally, the coating should be applied like paint.
- Coating must prevent coking (carburization of steel) and volatilization of Chromium.

<u>PROJECT PLANS AND PROGRESS</u>

11. **Past Accomplishments:**

General Accomplishments

- A family of preceramic polymers based on polysilsesquioxanes was chosen and tested to be able to provide the range of properties and chemistries to achieve corrosion resistant coatings in the Si-O-C(-N) range of compositions.
- The University of Central Florida accomplished initial characterization of the polymer-derived coatings.
- A low-cost route to produce the polysilsesquioxanes using a by-product of the RTV silicone industry (polymethylhydrosiloxane, PMHS) has been identified in collaboration with Dr. Yigal Blum of SRI.
- Appropriate reactive metal fillers (Al, Ti, and TiB_2) were identified by the University of Washington.
- PNNL identified SiC as an inert filler and Al-flake metal as a diffusion coating constituent.

- Larger coupons have been coated for testing by Air Products Research.
- Three program meetings with all participants and industrial partners have been held during the project duration.
- Presentations have been made at the 2002 Annual Meeting of ACerS, the 2003 Cocoa Beach Ceramics Meeting, and the 2003 Annual Meeting of ACerS, the 2004 Cocoa Beach Ceramics meeting, the 2004 Annual Meeting of ACerS (invited), HTCMC-5, the 2005 Cocoa Beach Ceramics Meeting, and the 2005 Annual Meeting of ACerS.

Task 1: Corrosion Resistant Compositions

- Milestone 1.1: Materials Selection of Polymers **(Completed)**
  Compositions in the range of Si-O-C-N with appropriate fillers were selected as corrosion resistant materials for protection against carburization and coking.
- Milestone 1.2: Selection of Filler Materials for Filled Polymer Coatings **(Completed)**
  SiC, $TiSi_2$, Al, Alumina, and stainless steel powders are being used to make coatings.
- Milestone 1.3: Corrosion Resistance Testing **(Completed)**
  All selected materials for the coatings have proven to have adequate corrosion resistance for these uses.

Task 2: Coating Engineering

- Milestone 2.1: Coating media preparation **(Completed)**
  Uses of organic solvents and painting, dipping or spraying coating techniques have been developed.
- Milestone 2.2: Polymer processing optimization **(Completed)**
  The processing parameters of particle-filled pre-ceramic polymers have been determined based on TGA/DTA results and pyrolysis experiments on stainless steel coupons.
- Milestone 2.3: Polymer-Filler Optimization **(Completed)**
  Development of processing methods to obtain durable, corrosion resistant coatings are completed and reproducible.
- Milestone 2.4: Coating Analysis and Optimization **(Completed)**
  The effect of the processing parameters on the microstructure and properties of the coatings has been completed and a robust set of processing parameters is in hand.

12. **Future Plans:**

Task 3: Characterization and Optimization for Service Environments

- Milestone 3.1 Coating Lifecycle Analysis **(Planned for FY-05 to FY-06)**
  Attractive coating materials will be analyzed from a life-cycle analysis perspective.
- Milestone 3.2 Laboratory Exposure Testing **(In Process)**
  This milestone will involve exposure of specimens to oxidative and corrosive environments (in laboratory furnaces) followed by detailed chemical and microstructural characterization using scanning electron microscopy (SEM), transmission electron microscopy (TEM), Energy Dispersion X-ray Analysis (EDAX), Auger electron microscopy (AEM), X-ray diffraction (XRD), weight gain/loss measurements etc.
- Milestone 3.3 Component coating **(In Process)**
  Components supplied by the industrial partners will be coated using the processes developed in Task 2 and Task 3 and meeting Milestone 3.2.
- Milestone 3.4 Field testing **(Planned for FY-05 and FY-06)**
  As a final task of the project in-service tests will be conducted. Coatings developed under Task 2 will be subject to a variety of industrially relevant environments.

13. **Project Changes:**

No major changes were made this year.

14. **Commercialization Potential, Plans, and Activities:**

The development of a liquid coating method based on a low-viscosity slurry or paint is the desired end product of this project. We anticipate working with the painting industry to further develop this technology such that an inexpensive coating solution for carburization and coking in the chemical process industry can be realized. We intend to supply Air Products research with enough material so that an adequate field test can be performed. A patent for our process (method and material) will be filed to ensure intellectual property rights.

15. **Patents, Publications, Presentations:**

An Invention Report on "Low-Cost Intermetallic Aluminide Coatings on Steels: Method and Product", Charles Henager, Jr., Yongsoon Shin, and William D. Samuels, PNNL was filed on December 20, 2004 and a **Patent Application** was filed on January 12, 2005.

A total of 21 presentations have been made for this project. The last several are included here. An invention report is being prepared for several of the coatings created for this project.

1. **C. H. Henager, Jr.**, Y. Shin, Y. D. Blum, L. A. Giannuzzi, S. M. Schwarz, "Environmental Barrier Coatings for Metals and Alloys using Particle-Filled Preceramic Polymers", Presented by Charles H. Henager, Jr. at ASM Materials Solutions Conference, Columbus, OH on October 19, 2004. **(INVITED)**
2. **C. H. Henager, Jr.**, Y. Shin, W. D. Samuels, A. L. Exarhos, L. A. Giannuzzi, S. M. Schwarz, and Y. Blum, "Environmental Barrier Coatings on SiC/SiC Composites using Filled Preceramic Polymers", Presented by Charles H. Henager, Jr. at 5th International Conference on High-Temperature Ceramic Matrix Composites (HTCMC 5), Seattle, WA on September 23, 2004.

Presented at the 29TH INTERNATIONAL CONFERENCE ON ADVANCED CERAMICS AND COMPOSITES, JANUARY 23-28, 2005, Cocoa Beach, Florida.

3. **Oxidation and degradation of SiC-filled preceramic polymer coatings**, CH Henager, Jr.*, Y Shin, PNNL, Richland, WA 99352, 509-376-1442; LA Giannuzzi, University of Central Florida, Orlando FL 32826; and SM Schwarz, University of Central Florida and NanoSpective, Inc., Orlando, FL 32826
4. **Reaction-diffusion Coatings using Al/Al_2O_3 filled preceramic polymers**, CH Henager, Jr.*, Y Shin, A Exarhos, PNNL, Richland, WA 99352, 509-376-1442; LA Giannuzzi, University of Central Florida, Orlando FL 32826; and SM Schwarz, University of Central Florida and NanoSpective, Inc., Orlando, FL 32826
5. **Coating Morphology, Microstructure, and Phase Content are Studied for Reaction-Diffusion Coatings Using Al/Al_2O_3 Filled Preceramic Polymers and SiC-Filled Preceramic Polymer Coatings,** S. M. Schwarz*, University of Central Florida, FL; CH Henager, Y Shin, AL Exarhos, Pacific Northwest National Laboratory, WA; LA Giannuzzi, FEI Company, OR.
6. **Optimization and Characterization of Polymer Derived Ceramic Coatings on Steel,** JD Torrey*, RK Bordia, University of Washington, WA; CH Henager, Pacific Northwest National Laboratory, WA.

Presented at the AMERICAN CERAMIC SOCIETY 107th Annual Meeting, April 10–13, 2005, Baltimore, Maryland

7. **Characterization of Polymer Derived Ceramic Coatings on Steel,** JD Torrey*, S Boddapati, CH Henager, Jr., and RK Bordia, University of Washington, WA.