1. **Project Name:** **ADVANCED COMPOSITE COATINGS FOR INDUSTRIES OF THE FUTURE**

2. **Lead Organization:** PNNL
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4. **Project Partners:**

1) University of Washington, subcontractor, Prof. Raj Bordia, 206-685-8158.
2) University of Central Florida, subcontractor, Prof. Lucille Giannuzzi 407-718-7708.
3) Air Products Research, Industrial Partner, In-kind labor, Dr. Eric Minford, 610-481-3248.
4) Solar Turbines, Partner, In-kind labor, Dr. Jeff Price, 619-544-5538.
5) Starfire Systems, Partner, In-kind labor, Dr. Walt Sherwood, 518-276-2112.
6) SRI, subcontractor, Dr. Yigal Blum (will be added in FY-04 and FY-05)

5. **Date Project Initiated and FY of Effort:** Project Initiated 10/1/2001 (FY-02), Current FY-03.

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

7. **Project Technical Milestones and Schedule:**

Task 1: Corrosion Resistant Compositions

- Milestone 1.1: Materials Selection of Polymers **(Completed)**
Compostions in the range of Si-O-C-N were selected as corrosion resistant materials for protection against carburization and coking. These materials are also amenable to coatings using preceramic polymers as prescribed in proposal.
- Milestone 1.2: Selection of Filler Materials for Filled Polymer Coatings **(In Process FY-03)**
Fillers are required to prevent crakcing and spalling of polymer-derived coatings. Selection of reactive and inert fillers will be made based on desired reactions, thermal porcessing, and corrosion resistance.
- Milestone 1.3: Corrosion Resistance Testing **(Planned for FY-04)**
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.

Task 2: Coating Engineering

Compositions that demonstrate corrosion resistance and physical properties (thermal expansion, thermal conductivity, etc.) within the range acceptable for further coating development will be applied to various substrates and the adhesion between the coating material and the substrates will be evaluated. Industrial partners helped select 316 stainless steel as our target substrate.

- Milestone 2.1: Coating media preparation **(Completed)**
Use of organic solvents and either spin coating or dip coating techniques have been developed.
- Milestone 2.2: Polymer processing optimization **(Completed)**

The processing paramters of four pre-cermaic polymers have been determined based on TGA/DTA results and pyrolysis experiemnts on stainless steel coupons.

- Milestone 2.3: Polymer-Filler Optimization **(In Process FY-03 to FY-05)**
  A major portion of the proposed work will be the development of processing methods to obtain durable, corrosion resistant coatings.
- Milestone 2.4: Coating Analysis and Optimization **(In Process FY-03 to FY-05)**
  The effect of the processing parameters on the microstructure and properties of the coatings will be studied. This and Milestone 2.3. will be closely coupled since the results of the characterization will be used to optimize the processing.

Task 3: Characterization and Optimization for Service Environments

The aim of this task is to study coatings behavior under service conditions. The industrial partners will be heavily engaged in this activity, either by performing benchmarking tests with their own facilities or advising PNNL on test conditions and analysis methods.

- Milestone 3.1 Coating Lifecycle Analysis **(Planned for FY-05 to FY-06)**
  Attractive coating materials will be analysed from a life-cycle analysis perspective to determine whether the cradle-to-grave benefits are acceptable. A Life-Cycle Design Assessment (LCDA) protocol is a structured approach for optimizing system performance while considering preferred raw materials, clean manufacturing technologies, quality of service requirements, and formulating competitive business strategies.
- Milestone 3.2 Laboratory Exposure Testing **(Planned for FY-04 to FY-05)**
  Coatings developed under Task 2 will be subject to a variety of industrially-relevant environments (including times, temperatures, stress levels, gas flow rates, etc.) and analysed using SEM, AEM, atomic force microscopy (AFM), etc.
- Milestone 3.3 Component coating **(Planned for FY-04 to FY-06)**
  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 to evaluate coatings performance in industrial environments.

8. Past Project Milestones and Accomplishments:

- A family of preceramic polymers based on polysilsesquioxanes have been 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.
- These polymers have been used to make thin, spin-on coatings on 316SS coupons by pyrolyzing at 700°C to 800°C in air, N2, Argon, or acetylene/argon mixtures.
- Initial characterization of the polymer-derived coatings has been accomplished by the University of Central Florida. See attached highlight.
- Controlled amounts of carbon can be achieved by selecting organic groups attached to polymer backbone. Choices range from methyl, ethyl, vinyl, propyl, and phenyl (listed in order of increasing carbon content) and controlled Si-O-C films can be obtained.
- A low-cost route to produce the polysilsesquioxanes using a by-product of the RTV silicone industry (polymethylhydridosiloxane, PMHS) has been identified in collaboration with Dr. Yigal Blum of SRI. This can be used to make an inexpensive slurry-based (paint) coating product that can be readily commercialized.
- Inexpensive chemical routes to add carbon to the PMHS starting polymers have also been identified by SRI and PNNL.
- Appropriate reactive metal fillers, Al, Ti, and TiB_2) have been identified by the University of Washington group for use as fillers in these systems.
- An in situ route to produce Ti_3SiC_2/SiC during polymer pyrolysis has been identified at PNNL. This has been shown to produce a tough ceramic product.

- Two program meetings with all participants and industrial partners have been held during the project duration. One was held in St. Louis (with the Annual Meeting of the American Ceramics Society) in 2002 and one in Nashville in 2003, again in conjunction with the Ceramics Society Annual Meeting.
- Presentations have been made at the 2002 Annual Meeting of ACerS, the 2003 Cocoa Beach Ceramics Meeting, and the 2003 Annual Meeting of ACerS.

9. Planned Future Milestones:

- We are in the process of writing a publication on our initial coating work. This will detail the use of polysilsesquioxanes containing methyl, propyl, and phenyl groups as protective spin-on coatings on 316 SS. **(Will be completed this year).**
- SRI and Dr. Yigal Blum will be brought on board in FY-04. **(Next year)**.
- The low-cost route to produce the polysilsesquioxanes from PMHS will be used to make a filled slurry-based coating product using a combination of commercial reactive and inert filler powders this year. Initial powder procurement has been accomplished. **(Will be completed in the next two years)**.
- Initial characterization of the <u>filled</u> polymer-derived coatings will be accomplished by the University of Central Florida this next year. **(Will be initiated this year)**.
- Controlled amounts of carbon additions to PMHS will be explored by selecting organic groups to attach to the PMHS polymer backbone. Choices range from methyl, ethyl, vinyl, propyl, and phenyl (listed in order of increasing carbon content) and controlled Si-O-C films will be obtained. **(Will be initiated this year)**.
- University of Washington group will use reactive metal fillers to make dense ceramic coatings. **(Will be initiated this year)**.
- An in situ route to produce Ti_3SiC_2/SiC during polymer pyrolysis using aluminum and TiC powder additions to PMHS polymers will be initiated this coming year. **(Will be initiated this year)**.
- Coating adherence and toughness will be measured at the University of Washington in FY-04 to FY-05 for all the coatings produced in this project. **(Future)**.
- Coating phase identification and microstructural characterization leading to coating optimization will be determined using the analytical tools at UCF and PNNL. **(Future)**.
- Laboratory corrosion testing of coated steel coupons will be initiated in FY-04. **(Future)**.
- Industrial partner corrosion testing, filed testing, and component coating and testing will be initiated in FY-05. **(Future)**.
- A route to commercialization of our slurry-based (paint) coating will be developed during FY-05 and brought to completion in FY-06 as planned. **(Future)**.

10. Issues/Barriers:

- The issue of cast has been addressed by aggressively pursuing a low-cost precursor to the desired preceramic polymers. By teaming with SRI and Dr. Yigal Blum we have moved from using materials that cost \$100/lb to materials that cost \$10/lb and that can go much lower in cost for bulk purchases.
- A technical barrier that remains to be overcome is the matching of the coating coefficient of thermal expansion (CTE) to that of the substrate. The use of a range of available filler materials suggests that this can be done but we anticipate a bit of iteration on this.
- A barrier that we have not yet discussed will be to be able to apply our coating process to the ID of steel tubing in such a way that attachments of the tubing can still be made. Dr. Eric Minford points out that welding of coated tubes presents a problem. We intend to work closely with our industrial partners to overcome this barrier. We desire to develop an in situ coating technique that can be used to coat already joined piping.

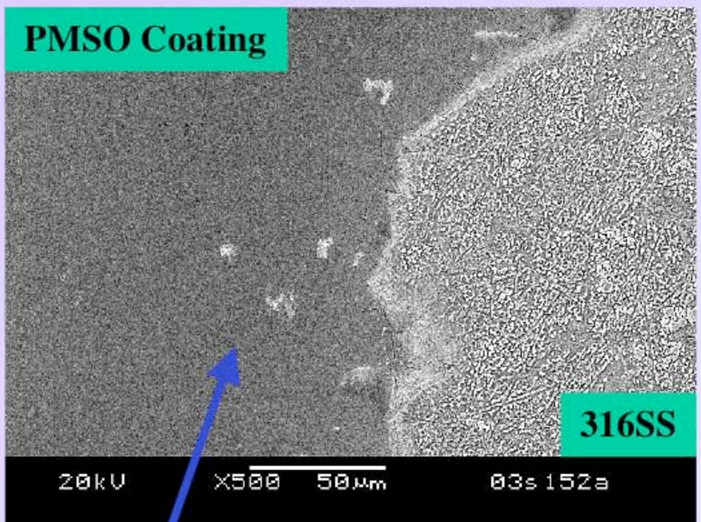
11. **Intended Market and Commercialization Plans/Progress:**

- 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.

12. **Patents, publications, presentations:**

1. L. A. Giannuzzi, "FIB specimen preparation: The lift out method", presented at the 2002 Annual Meeting of the American Ceramics Society, St. Louis, MO, April 30, 2002.
2. C. H. Henager, Jr. and Y. Shin, "Environmental Barrier Coatings on Metals and Ceramics Using Preceramic Polymers," presented at the 27th Annual Cocoa Beach Ceramics conference, January 26-31, 2003.
3. B. W. Kempshall, C. H. Henager, Jr., L. A. Giannuzzi, "Microstructural Evaluation of Environmental Barrier Coatings on Metals and Ceramics Using Preceramic Polymers," presented at the 27th Annual Cocoa Beach Ceramics conference, January 26-31, 2003.
4. J. D. Torrey, R. K. Bordia, M. Stackpoole, and C. H. Henager, Jr., "Reactive Metal Filled Preceramic Polymers as Precursors for Ceramic Coatings," presented at the 27th Annual Cocoa Beach Ceramics conference, January 26-31, 2003.
5. C. H. Henager, Jr., B. W Kempshall, and L. A. Giannuzzi, "Characterization and analysis of interfaces between SiC and Ti3SiC2/SiC composites formed during reactive joining," presented at the 2003 Annual Meeting of the American Ceramics Society, Nashville, TN, April 29, 2003.
6. S. M. Schwarz, B. W. Kempshall, C. H. Henager, Jr., and L. A. Giannuzzi, "Microstructural Evaluation of Environmental Barrier Coatings on Various Substrates Metals and Ceramics Using Preceramic Polymers," presented at the 2003 Annual Meeting of the American Ceramics Society, Nashville, TN, April 29, 2003.

Si-O-C Protective Coating on 316SS from polymethylsilsesquioxane (PMSO) polymers



- Coating prepared by dip coating metal in polymer in solution.
- Pyrolysis at 700˚C in Ar, N_2, or Air.
- Protective and crack-free when thin.
- Will require reactive fillers when thicker coatings desired.

- Advanced analysis using FIB-TEM* allows detailed study of coating in cross-section.
- Small nano-precipitates (carbon?) observed in coating.
- Compositional profile indicates strong interaction with substrate.

* focused ion beam preparation and transmission electron microscopy