ADMINISTRATIVE INFORMATION

1. **Project Name:** High-Performance, Oxide-Dispersion-Strengthened Tubes For Production of Ethylene and Other Industrial Chemicals

2. **Lead Organization:** Michigan Technological University
Institute of Materials Processing
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3. **Principal Investigator:** Marvin G. McKimpson
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4. **Project Partners:** Special Metals Corporation—Huntington, WV
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5. **Date Project Initiated:** September 30, 2001

6. **Expected Completion Date:** September 29, 2004

PROJECT RATIONALE AND STRATEGY

7. **Project Objective:** (Please provide 1-2 sentences describing the objective of this project.)

This project seeks to develop creep-resistant, coking-resistant oxide-dispersion-strengthened (ODS) tubing for use in industrial-scale ethylene pyrolysis and steam methane reforming operations. In short-residence-time ethylene pyrolysis furnaces, this novel tubing is expected to at least double the time period that a furnace can run before being shut down for decoking. The technology also has potential for increasing the maximum allowable service temperature of the pyrolysis tubing.

8. **Technical Barrier(s) Being Addressed:** (Please provide 1-3 sentences describing the problem(s) and/or barrier(s) limiting industrial energy efficiency which this project is addressing.)
1-2 sentences

In 2002, there were 44 domestic ethylene production facilities, having total combined (nameplate) capacity of 29.3 million tonnes/year. Coking--the buildup of carbon residue on the inner surface of pyrolysis furnace tubes--is a major concern for these ethylene producers. This carbon buildup reduces energy efficiency and increases production of greenhouse gases by:

- Retarding heat transfer to the reactant gases and heat recovery systems,
- Requiring additional energy for pumping of ethylene feedstocks through the partially-restricted furnace tubes,
- Consuming carbon which could otherwise be converted into useful products, and
- Requiring additional energy for tube decoking.

Furnaces must be shut down every 20 to 60 days for decoking at a cost on the order of $9 million per year in lost production per plant. Reactor tubes also need to be replaced every 3 to 5 years at a cost on the order of ~$1 million per installation. Aluminum-rich tubing alloys have been shown to reduce coking by at least factor of 2, but current alloys require unacceptable trade-offs in elevated temperature creep strength, ductility or fabricability (especially weldability).

9. **Project Pathway:** (Please provide a one-paragraph summary of the approach, or pathway, being used to address the barrier(s). Emphasize the overall strategic approach for the project, not individual R&D tasks.)

This project is developing co-extruded pyrolysis tubing with an inner core of Incoloy® MA 956 surrounded by an outer cladding of a new oxide-dispersion-strengthened (ODS) variant of Incoloy® Alloy 803. Incoloy® MA 956 has excellent creep resistance and adequate aluminum for substantially reduced coking, but exhibits limited ductility and weldability. The new ODS Alloy 803 being developed will provide creep strength comparable to Incoloy® MA956 coupled with the improved ductility and weldability of an austenitic pyrolysis tubing alloy. Combining the two materials will provide a clad tube with the coking resistance, creep resistance and ductility/fabricability needed for industrial service. To minimize cost, this tubing will be produced by direct powder co-extrusion, eliminating one fabrication operation.

10. **Critical Technical Metrics:** (Please indicate how success or failure will be measured for this project by stating the baseline technical metric(s) and the metric(s) needed for realization of the project objectives.)

This project seeks to develop ODS Alloy 803 material exhibiting elevated temperature strength comparable to Incoloy® MA956 and to demonstrate that Incoloy® MA 956/ODS Alloy 803 tubes:

- Can be fabricated successfully by direct powder co-extrusion into products exhibiting uniform cladding thickness and good bonding between the ferritic Incoloy® MA 956 and austenitic ODS Alloy 803.
- Will exhibit at least a factor of two decrease in the rate of coking compared to existing commercial wrought materials such as Incoloy® 800.
- Can be joined successfully to produce joints having strength comparable to current radiant coil materials.

PROJECT PLANS AND PROGRESS

11. **Past Accomplishments:** (Please summarize the major accomplishments and **key** milestones achieved to date. Note: May not be applicable for projects initiated in FY04.)

During the first two years of the program, an instrumented mechanical alloying system was constructed and used to develop a protocol for producing ODS Alloy 803 powder. Practices for fabricating this powder into bar were also developed and several generations of extruded ODS alloy 803 material have been produced and evaluated. First-generation co-extruded Incoloy® MA 956/ODS Alloy 803 tube was also fabricated and evaluated. Elevated temperature flow stress data was obtained on both the Incoloy® MA 596 and ODS Alloy 803 materials in the as-extruded (unrecrystallized) condition and used as input for developing a finite element model of the direct powder co-extrusion process. More recently, this finite element model has highlighted important issues for successful extrusion of a thick powder cladding on solid tubular core. A laboratory test rig has also been set up for coking deposition studies on Incoloy® MA 956 in both the normal and pre-treated conditions. The first experimental heats of a modified ODS Alloy 803 material designed to facilitate fusion welding have also been produced.

12. **Future Plans:** (Please summarize the **key** milestones and deliverables with dates for the life of this project. A comprehensive activities schedule is not required.)

During FY04, this program was restructured so that a complete package of technical work will be completed by 30 September 2004. This revised plan involves work in five areas:

- **Technology commercialization.** Current ethylene producers and ethylene furnace manufacturers are being reviewed and contacted to compile additional information about the suite of properties which the oxide dispersions strengthened (ODS) tubes must exhibit in order to be commercially viable. Performance and cost information will be integrated into a spreadsheet model to facilitate assessment of tradeoffs between material performance and cost. Once this model is developed, it will be reviewed with ethylene industry personnel and used to help recruit additional development team members.

- **Coking characteristics of Incoloy® MA 956**. The laboratory-scale coking test rig set up at Michigan Technological University is being used to make a comparative assessment of the coking characteristics of Incoloy® MA 956 and existing commercial alloys such as Incoloy® 800. This work is being done with the assistance of Dr. Lyle Albright of Purdue University. In addition, studies will be carried out to assess the potential benefits of controlled oxidation pretreatments for Incoloy® MA 956. An MPLUS proposal has also been submitted to Oak Ridge National Laboratory for performing coking tests on the co-extruded tube using the ORNL high-flow-rate coking apparatus. If approved, this work will also be completed by 30 September.

- **Joining of ODS tubes.** This work will involve three major activities. First, existing joining technologies for ODS alloys are being assessed, including recent concepts developed by JCG Corporation, safe-end joints, and threaded joints. Second, feasibility studies are being conducted on slight modifications of the ODS Alloy 803 which have potential for greatly facilitating fusion-based joining techniques. Third, arc welding studies are being conducted on dissimilar-metal Incoloy® MA 956/ODS Alloy 803 joints following the approach called out in the original proposal.

- **Elevated temperature properties of ODS Alloy 803**. One additional lot of ODS Alloy 803 extruded bar stock is being produced and evaluated in an effort to further develop high-temperature properties of this new alloy. This final generation of material will be subjected to ambient-temperature tensile testing at Michigan Technological University and elevated temperature creep, oxidation and carburization testing at Special Metals.

- **Fabrication of bimetallic Incoloy® MA 956/ODS Alloy 803 tubes.** Two additional generations of Incoloy® MA 956/ODS Alloy 803 tubes will be produced. The final-generation tube will be produced using the same ODS Alloy 803 powder as that subjected to elevated-temperature testing. The fabricated tube will be assessed for powder recrystallization characteristics and geometric uniformity.

13. **Project Changes:** (Please describe changes in scope, approach or schedule during the past year in response to any unforeseen problems/issues or successes.)

In addition to the project restructuring described above, potential users of the clad pyrolysis tubing have suggested that the inner core of Incoloy® MA 956 should be thicker than initially envisioned. This affected both the tube fabrication and joining work. It required that new, heavier-wall Incoloy® MA956 precursor tube be fabricated, highlighted the need for the current powder co-extrusion simulation effort, and triggered development of the current ODS Alloy 803 modifications designed to facilitate fusion welding. Ongoing industrial interest in the ANK 400 anti-coking technology from Nova Chemical and Kubota has also caused the program to be slightly revised to provide greater emphasis on characterizing and understanding the surface oxides which develop on the Incoloy® MA 956 during pyrolysis service.

14. **Commercialization Potential, Plans, and Activities:** Describe the end-use application and market potential for the project, and the plans, progress, and partners for commercial application/adoption, where appropriate; identify what the product of the project will be and how this product will be introduced/disseminated to industry.)

The co-extruded tubes being developed are expected to be useful for both ethylene pyrolysis furnaces and steam reforming operations such as those used to produce ammonia, hydrogen and methanol. In 2000, the estimated North American market for such tubes was 5600 tonnes/year and the estimated worldwide market was 20,000 tonnes/year. Special Metals is currently an established supplier of wrought furnace tubes for these markets. The data package developed under this program will be reviewed with furnace manufacturers and producer organizations, and will provide a foundation for recruiting additional team members for further technology development. Other high-temperature spin-off applications for the ODS Alloy 803 material developed under the program will also be explored.

15. **Patents, Publications, Presentations:** (Please list number and reference, if applicable. If more than 10, please list only 10 most recent.)

1. M. G. McKimpson and M. T. King, "Instrumented Mechanical Alloying of a Novel Superalloy Powder". Presented at Materials Science & Technology 2003 (Chicago, IL, November 12, 2003) and published in F. Marquis, ed., *Powder Materials: Current Research and Industrial Applications III*, Warrendale, PA, TMS, 2003. pp. 273-289.
2. M. G. McKimpson, "High Performance Oxide-Dispersion-Strengthened Tubes for Production of Ethylene and Other Industrial Chemicals". Presentation at MTI Fall meeting (San Antonio, TX, 21 October 2003.)
3. M. G. McKimpson and M. T. King, "Development of Co-Extruded, Oxide Dispersion Strengthened Tubes for Ethylene Pyrolysis". Accepted for presentation in the Product Application and Development Symposium at MS&T 04 (26-30 Sept. 2004; New Orleans LA) and publication in the proceedings of that symposium.
4. Abstract describing the coking work is being submitted for presentation at the annual American Chemical Society meeting (Philadelphia PA, Aug. 22-26 2004)