Final Technical Report

High-Performance, Oxide-Dispersion- Strengthened Tubes for Production of Ethylene and Other Industrial Chemicals

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1.0 Executive Summary

This project was undertaken by Michigan Technological University and Special Metals Corporation to develop creep-resistant, coking-resistant oxide-dispersion-strengthened (ODS) tubes for use in industrial-scale ethylene pyrolysis and steam methane reforming operations. Financial support for the program was provided by the Office of Industrial Technologies of the U.S. Department of Energy.

Ethylene pyrolysis tubes are exposed to some of the most severe service conditions for metallic materials found anywhere in the chemical process industries, including elevated temperatures, oxidizing atmospheres and high carbon potentials. During service, hard deposits of carbon (coke) build up on the inner wall of the tube, reducing heat transfer and restricting the flow of the hydrocarbon feedstocks. About every 20 to 60 days, the reactor must be taken off-line and “decoked” by burning out the accumulated carbon. This decoking costs on the order of \$9 million per year per ethylene plant, accelerates tube degradation, and requires that tubes be replaced about every 5 years.

The technology developed under this program seeks to reduce the energy and economic cost of coking by creating novel bimetallic tubes offering a combination of improved coking resistance, creep resistance and fabricability not available in current single-alloy tubes. The inner core of this tube consists of Incoloy[®] MA956, a commercial ferritic Fe-Cr-Al alloy offering a 50% reduction in coke buildup combined with improved carburization resistance. The outer sheath consists of a new material—oxide dispersion strengthened (ODS) Alloy 803—developed under the program. This new alloy retains the good fireside environmental resistance of Alloy 803, a commercial wrought alloy currently used for ethylene production, and provides an austenitic “casing” to alleviate the inherently-limited fabricability of the ferritic Incoloy[®] MA956 core. To provide mechanical compatibility between the two alloys and maximize creep resistance of the bimetallic tube, both the inner Incoloy[®] MA956 and the outer ODS Alloy 803 are oxide dispersion strengthened materials produced using mechanical alloying technology. To minimize cost, the bimetallic tube is produced by direct powder co-extrusion.

This technology has potential for domestic energy savings of up to 4.1 trillion BTU/year (4.3×10^{15} J/year) and a reduction of 370,000 tons (340,000 tonnes) of CO₂ emissions in short-residence-time ethylene furnaces. This represents an energy savings and CO₂ emissions reduction of about 3.3%. If the technology is also applied to other types of ethylene pyrolysis furnaces, total energy savings and CO₂ emissions reductions could increase by up to five times.

The work involved:

- Developing powder and consolidation processing protocols to produce an oxide-dispersion strengthened variant of Alloy 803 exhibiting creep strength comparable to Incoloy[®] Alloy MA956,
- Developing a direct powder co-extrusion protocol for fabricating co-extruded bimetallic Incoloy[®] Alloy MA956 / ODS Alloy 803 tubes,
- Characterizing the properties of the ODS Alloy 803 material, the welding characteristics of the bimetallic tubes, and the coking characteristics of the Incoloy[®] MA956 alloy, and
- Documenting the potential energy savings and user requirements for these bimetallic pyrolysis furnace tubes.

The project demonstrated that oxide dispersion strengthened Alloy 803 can be produced successfully using conventional mechanical alloying technology. Processed material can be recrystallized to a largely coarse-grained microstructure by annealing at 1300°C for 1 hour. Both finite element simulation and experimental trials showed that bimetallic ODS Alloy 803 / Incoloy[®] Alloy MA956 tubes can be produced by direct powder co-extrusion using a powder/powder approach in which concentric rings of Incoloy[®] MA956 powder and ODS Alloy 803 powder contained in a tubular can are direct-extruded using a mandrel. Coking tests confirmed that pre-oxidized Incoloy[®] MA956 exhibits at least a 50% lower rate of coke buildup than chromia-forming alloys such as Incoloy[®] 800. Mass change measurements showed the rate of coke buildup on the Incoloy[®] MA956 in an equimolar N-butane/steam mixture at 800°C was about 1/3 that observed on the Incoloy[®] 800 over a 7-hour test period.

The oxide dispersion strengthened bimetallic radiant coil technology explored under this program has significant potential for energy savings and productivity improvements for domestic ethylene producers. In today's competitive market, however, domestic furnace manufacturers and ethylene producers appear reluctant to pay any cost premium for higher-performance coil materials offering either higher temperature capabilities or longer service life. Interest in oxide dispersion strengthened radiant coils is likely to increase if furnace and ethylene producers begin to focus more on increasing tube wall temperatures to improve productivity.

Any future development work on oxide dispersion strengthened pyrolysis tubing should be undertaken using a consortium approach involving a broad range of stakeholders, including ethylene producers, furnace manufacturers, material producers and research organizations.

2.0 Introduction

Ethylene (C_2H_4) is one of the most widely used of all industrial chemicals. It is a colorless, flammable, man-made gas used as the starting stock for a wide range of common polymers and petrochemicals, including polyethylene, polyester, polyvinyl chloride, polystyrene, ethanol and ethylene glycol. In 2002, US production of ethylene was about 55 billion lbs, representing about one fourth of the total global production.¹ Manufacturing of ethylene is also extremely energy-intensive. Ethylene production requires the largest amount of process energy of any of the top 15 industrial chemicals.² In 2002, total energy usage for ethylene production was about 620 trillion BTU (650×10^{15} J).³ Fortunately, the process also has excellent potential for improved energy efficiency; ethylene production has been ranked second highest of all the major industrial chemical processes (after chlorine and sodium hydroxide) in potential for additional energy savings based on thermodynamic requirements.² Current ethylene conversion technology requires high processing temperatures, and any enhancements which improve the efficiency of these high temperature operations will have a significant impact on overall energy usage.

2.1 Technology Benefits

In 2001, researchers at Michigan Technological University (Houghton, MI) and Special Metals Corporation/Huntington Alloys (Huntington, WV) initiated a program to develop improved superalloy tubes for commercial production of ethylene and other industrial chemicals. The work was sponsored by the Office of Industrial Technologies, Energy Efficiency and Renewable Energy, U.S. Department of Energy. The goal of the program was to develop a novel bimetallic tube for high temperature furnace reactors which could reduce tube coking (fouling) by a factor of 2 and also extend tube service lives by a factor of 2.

Ethylene pyrolysis tubes are exposed to some of the most severe service conditions for metallic materials found anywhere in the chemical process industries, including elevated temperatures, oxidizing atmospheres and high carbon potentials. During service, hard, tightly-adhering deposits of carbon termed “coke” also build up on the inner wall of the tube, reducing heat transfer, restricting the flow of the hydrocarbon feedstocks and necessitating increases in operating pressure. These coke deposits are so severe that the pyrolysis reactor must be taken off-line and “decoked” about every 20 to 60 days by burning out the accumulated carbon using either air or steam. This decoking costs on the order of \$9 million per year per ethylene plant. It also accelerates tube degradation and contributes to the need for replacing tubes about every 5 years.

The pyrolysis tube technology developed under the program seeks to reduce the energy and economic cost of coking by creating novel bimetallic tubes offering a combination of improved coking resistance, creep resistance and fabricability not available in current single-alloy tubes. The inner core of this tube consists of Incoloy[®] MA956, a commercial ferritic Fe-Cr-Al alloy offering a 50% reduction in coke buildup combined with improved carburization resistance. The outer sheath consists of a new material—oxide dispersion strengthened (ODS) Alloy 803—developed under the program. This new alloy retains the good fireside environmental resistance of Alloy 803, a commercial wrought alloy currently used for ethylene production, and provides an austenitic “casing” to alleviate the inherently limited fabricability of the ferritic Incoloy[®] MA956 core. To provide mechanical compatibility between the two alloys and maximize creep resistance of the bimetallic tube, both the inner Incoloy[®] MA956 and the outer ODS Alloy 803

are oxide dispersion strengthened materials produced using mechanical alloying technology. To minimize cost, the bimetallic tube is produced by direct powder co-extrusion. Nominal compositions of both Incoloy® MA956 and ODS Alloy 803 are listed in Table 1.

Initially, the bimetallic tubes will be most applicable to short-residence-time ethylene furnaces such as those used to process naphtha feedstocks. Such feedstocks currently represent about 20% of domestic ethylene production. In these furnaces, the technology has potential energy savings of 4.1 trillion BTU (4.3×10^{15} J) per year. This also represents a reduction of 370,000 tons (340,000 metric tons) of CO₂ emissions per year. Over the longer run, these bimetallic tubes also have potential for reducing coking in furnaces using ethane, propane/butane, gas oil or other feedstocks. Use of the bimetallic tube technology in these other facilities can increase energy saving and CO₂ emission benefits by up to a factor of five, representing an energy savings of 20 trillion BTU/year (21×10^{15} J/year) and a reduction of 1.9 million tons (1.7 million metric tons) in CO₂ emissions per year.

The bimetallic tubes also have potential for enabling temperature increases of 55°C-65°C in ethylene furnace operating temperatures in new facilities. This increased temperature capability will permit furnace designers to develop higher-severity ethylene cracking furnaces, allowing higher furnace throughputs and/or greater selectivity for ethylene vs. other heavier furnace products. This can be significant for ethylene producers. Based on the literature, furnace productivity can increase by up to 30 wt% for a 55°C increase in furnace outlet temperature.⁴

Although this program focused primarily on developing tubes for the ethylene industry, the technology developed can also be valuable for steam reforming operations such as those used to produce hydrogen, ammonia and methanol. For ammonia, hydrogen and methanol producers, the major economic benefits will be to reduce lost production time due to tube replacement, reduce the cost of replacement tubing, and increase reactor productivity due to the larger diameter and/or thinner-walled tubes made possible by higher strength alloys. Schillmoller notes that reformer furnace tubes used in the ammonia industry typically exhibit lifetimes of about 10 years and that the annual North American requirement for replacement reformer tubing was approximately 2600 tons/yr in 2000. The total annual market worldwide for pyrolysis and reformer tubing (both maintenance and new construction) was estimated to be 22,000 tons that year.⁵ The excellent environmental resistance of the bimetallic tubes being developed should lead to an increase in service life—probably by a factor of two—over existing conventional materials for both pyrolysis and reformer applications. The new alloy developed for the outer sheath of the bimetallic tube is also attractive as a candidate material for fixtures and tooling in the heat treatment and metalworking industries due to its combination of high elevated temperature strength and good environmental resistance.

Table 1. Composition of Selected Alloys (Wt%)									
Alloy	Fe	Ni	Cr	Al	Ti	Si	C	Y₂O₃	Other
Incoloy® MA956	74.0	-	20.0	4.5	0.5	-	0.05	0.5	-
ODS Alloy 803	36.0	37.0	26.0	0.3	0.3	0.8	0.08	0.5	0.8 Mn
HP Mod-Nb	37.0	35.0	25.0	-	-	1.8	0.45	-	1.0 Nb
HP Mod-Nb MA	37.0	35.0	25.0	-	-	1.8	0.45	-	1.0Nb, trace Ti, Zr and/or Rare Earths

2.2 Technical Approach

The tubes developed under the program are shown schematically in Figure 1. The inner core is Incoloy[®] MA956, a commercial iron-base oxide dispersion strengthened material produced by Special Metals. It is made by mechanical alloying, a solid state milling process in which nanometer-sized oxide particles are uniformly dispersed in the metal. The outer sheath is a creep-resistant, oxide-dispersion-strengthened variant of Incoloy[®] Alloy 803 developed under the program. Nominal compositions of both alloys are listed in Table 1.

Figure 1. Schematic of bimetallic extruded tube developed under the program.

Note that Incoloy[®] MA956 is a ferritic material containing 20% Cr and 4.5% Al. At elevated temperatures, most superalloys form a protective oxide scale consisting primarily of chromium oxide. In contrast, Incoloy[®] MA956 forms a duplex protective scale consisting of an outer layer of chromium oxide with an inner, more chemically stable layer of alumina. This duplex oxide confers excellent environmental resistance to both oxidation and carburization.⁶ The limited data available at the start of the program suggested that this Al₂O₃-rich scale would give Incoloy[®] MA956 substantially better coking resistance than currently-used pyrolysis furnace alloys such as centrifugally cast microalloyed HP-Mod Nb (HP-Mod Nb MA) materials. (See Table 1.)

Unfortunately, Incoloy[®] MA956 is difficult to fusion weld and exhibits only limited ductility at ambient temperature, making it challenging to use for field fabrication of commercial ethylene furnaces. Incoloy[®] Alloy 803 is an austenitic alloy which can be readily welded and is currently used in commercial high-severity ethylene furnaces. The creep strength of Alloy 803 (and all other currently-used pyrolysis furnace alloys), however, is substantially lower than that of Incoloy[®] MA956. By developing an oxide dispersion strengthened variant of Incoloy[®] Alloy 803 having creep strength comparable to Incoloy[®] MA956 and using this new material as an outer sheath for the Incoloy[®] MA956, one can obtain a bimetallic tube exhibiting the benefits of both materials.

2.3 Development Team

Michigan Technological University, the lead organization and university partner on the program, has special expertise and capabilities for producing mechanically alloyed materials. University personnel have been processing kilogram-sized lots of these alloys for more than a decade. Special facilities include several oil-cooled attritors for mechanical alloying (ranging in capacity from 50 g up to 18 kg), an inert-atmosphere powder processing system which allows powders to be handled, milled and consolidated without atmospheric exposure, and equipment for high-pressure powder consolidation. Typical programs have included: 1) Developing diffusion bonding methods for mechanically alloyed Inconel[®] Alloy MA 754, 2) Developing mechanically alloyed precursors for superconducting wires and scaling up production of these precursors to kilogram quantities, and 3) Producing kilogram-sized lots of experimental ODS nickel-base alloys for elevated temperature propulsion systems. These nickel alloys were milled in a 1-S attritor, consolidated by extrusion or hot isostatic pressing, annealed and characterized.

Michigan Technological University was also a member of the Huntington Alloys Vision 21 project team working to develop enhanced Incoloy[®] Alloy MA956 tubing for high temperature heat exchangers.

Special Metals Corporation/Huntington Alloys, the industrial partner in the program, is one of two commercial suppliers world-wide of mechanically alloyed high temperature superalloys. Indeed, Special Metals personnel invented and first commercialized mechanical alloying technology about three decades ago.* The organization has production-scale mechanical alloying facilities in both Kentucky and the United Kingdom, and regularly supplies both iron- and nickel-based oxide dispersion strengthened alloys for defense and industrial applications.

Special Metals contributed to this program in a number of important ways. The twelve extrusions required under the program were all done on the 750T extrusion press located in the Special Metals Technology Processing Center at Huntington. Special Metals also provided the custom mandrels and dies required for the bimetallic tube extrusions.

In addition, the organization supplied Incoloy[®] MA956 tubes for the initial bimetallic tube extrusion trials, as well as over 30 kg of commercial Incoloy[®] MA956 powder for later work. They provided chemical and microstructural characterization of the oxide dispersion strengthened (ODS) Alloy 803 material, as well as stress rupture testing of the final ODS Alloy 803 extrusions developed under the program. In addition, the group contributed technical assistance in a number areas, including extrusion practices, secondary recrystallization of the ODS Alloy 803, and powder/powder tube extrusions. They also supplied supplementary materials for these powder/powder extrusions. In addition, Special Metals personnel provided commercialization assistance in a number of areas, including collecting market assessment information from current pyrolysis tubing customers, presenting the clad tube concept to potential users, providing background information on coking issues in commercial ethylene facilities, and facilitating attendance at a Materials Technology Institute meeting. All of these items were provided as in-kind cost sharing to the program.

* Mechanical alloying technology was originally developed by Inco Alloys at their corporate research facility in New York. This facility was then moved to Huntington WV, and was subsequently purchased by Special Metals.

3.0 Background

Industrial ethylene is produced by pyrolysis (cracking) of hydrocarbons in the presence of steam. It is carried out in large, multiple-tube furnaces operating at temperatures up to 1149°C (2100°F). Hydrocarbon feedstocks—typically ethane (42%), propane/butane (25%), naphtha (20%) or gas oil (10%)—are mixed with steam and injected into the pyrolysis furnace. On heating, the hydrocarbon reacts to form ethylene, releasing hydrogen. The amount of ethylene formed (i.e. the conversion efficiency) depends on the feedstock and process conditions. For ethane, up to 80% of the feedstock may be converted into ethylene; for a heavier material such as gas oil, conversion yields may be about 25%. Maximum production of ethylene generally requires low operating pressures (inlet pressures of typically 370-640 kPa), high tube wall temperatures (typically 1040-1120°C), and low residence times (typically 0.15-0.5 s).

After cracking, the reacted gas is quenched and compressed for separation. Caustic scrubbing removes hydrogen sulfide and carbon dioxide. The gas is chilled to remove moisture and passed through distillation columns to remove methane and ethane. Acetylene is generally separated by selective hydrogenation. Hydrocarbon wastes are routed back to the pyrolysis furnace and burned to provide much of the heat needed for the pyrolysis operation.

3.1 Material Requirements

The vertically-mounted radiant tubes (“radiant coils”) used in ethylene pyrolysis furnaces are exposed to some of the most severe service conditions for metallic materials used anywhere in the chemical process industries. Tube metallurgy currently limits furnace design, and successful tube performance depends on several criteria, including:

- **Coking resistance:** As hydrocarbon feeds are being pyrolyzed, a portion of the reacting carbon accumulates on the inner wall of the tube. These coke deposits reduce heat transfer through the tube walls and restrict the flow of feed gas through the tube. Eventually this buildup becomes so great that the reactor must be taken off-line and “decoked” by burning out the accumulated carbon using either steam or air. Alloy surface chemistry plays a key role in determining the amount of coke buildup. High temperature alloys generally rely on a durable, compact protective surface oxide to control environmental degradation. The composition of this oxide can have a significant impact on the rate of coke buildup. Similarly, anything which disrupts this oxide to expose metallic iron or nickel will markedly accelerate coking.
- **Oxidation resistance:** During heat-up, cool-down and decoking, as well as during other process transients, the hot tubes are exposed to air or other oxidizing environments. As with coking, the composition of the protective surface oxide has a major impact on the oxidation resistance of the material. Current pyrolysis tube alloys rely on an oxide scale containing predominantly chromia, although Incoloy[®] MA956, due to its higher aluminum content, forms a more stable mixed chromia/alumina scale. Elements such as manganese, silicon and rare earth metals may also contribute to effective oxidation and coking resistance.

- **Carburization resistance:** If the protective surface oxide is destroyed, carbon from the hydrocarbon feedstock will diffuse into the surface of the tube during service. This carbon penetration forms internal carbides, reducing the ductility of the material and making it more sensitive to damage from either bending moments or thermal cycling. The rate of carburization depends on alloy chemistry, but roughly doubles for each 55°C (100°F) increase in operating temperature.⁷ It is generally agreed that frequent decoking promotes carburization and shortens overall tube life.
- **Creep resistance:** High creep resistance also helps maintain protective surface oxides, improving coking, oxidation and carburization resistance. Creep rupture strength is also the primary criteria determining tube wall thickness, and most tubes are sized based on 100,000 hour stress rupture performance. High creep strength is clearly desirable to minimize wall thickness and maximize the heat flux through the tube into the reacting hydrocarbons. High creep resistance is particularly important because one of the major ways to improve ethylene process selectivity and productivity is to increase temperature and reduce residence time within the hot zone of the reactor. It is estimated that a 50°C increase in operating temperature will improve ethylene yield by 30%.⁸
- **Weldability and field fabricability:** Due to the high service temperatures and severe coking/carburization experienced by pyrolysis tubes, these tubes must be replaced periodically—typically about every five years.⁵ Accordingly, the alloys must be able to be welded readily.
- **Cost:** Tubing cost—particularly since tubes must be replaced periodically—represents a significant expense. For ethylene production, the pyrolysis furnace typically represents 10-20% of the total capital cost of a plant, and tubes represent about one third of this furnace cost.⁹

All of these criteria are important, but it is generally agreed that coking resistance and creep resistance have the greatest impact on tubing performance.

3.2 Current Coil Technology

The first pyrolysis reactors built in the early 1950's were small-capacity units with horizontally-tubed furnaces made using AISI Type 304 stainless tubing. Over the next 30 years, both tube diameters and maximum operating temperatures steadily increased, requiring more robust materials. Preferred alloys progressed through AISI 310 SS, Alloy 800 and cast alloys HK-40 and HP45. By the 1980's, a somewhat stronger cast HP45 alloy containing about 1% Nb and 2% Si (HP45 Mod Nb) was being used in the vertical furnaces then under construction. This alloy has now been largely displaced by HP45 ModNb MA, a similar cast alloy containing low level "Micro-Alloying additions" of Ti, Zr and/or rare earth elements to refine carbide structure and further improve creep resistance.

The industry continues to look for improved materials and technologies to enable them to move toward increasingly severe cracking conditions (higher temperatures, shorter residence times and lower partial pressures of product) in order to increase ethylene yields. Cast alloys containing 35%Cr and 45%Ni are being considered for some installations, since both Cr and Ni tend to improve both creep strength and coking resistance.⁴ There is also a renewed interest in wrought tubular materials such as Incoloy[®] Alloy 803, since plant designers are moving to both smaller

diameter (e.g. 25 mm – 75 mm) and internally-finned tubes to maximize heat transfer to the flowing hydrocarbon feed.

Several approaches have been adopted to minimize coking in radiant coils. Proprietary coating technologies have been marketed by several organizations, including Alon Surface Technologies, Inc., Westaim Surface Engineered Products, and Daido Steel in collaboration with the Royal Dutch Shell group.¹⁰ All of these technologies provide thin coatings with low levels of Ni and Fe on the surface to reduce coke buildup. Some contain multiple layers to reduce diffusion effects, and most appear to reduce coking by a factor of 2 to 3. Other ethylene producers use various additives to minimize coking. Producers using ethane- or propane-based feedstocks will often add sulfur-bearing compounds such as hydrogen sulfide, dimethyl sulfide or mercaptans. It is generally believed that these additives work by decomposing to elemental sulfur. This elemental sulfur then converts oxides to sulfides and/or forms protective sulfide films over exposed metal surfaces. A variety of other proprietary additives, including tin-silicon, organo-phosphorus and silica/sulfur+dimethydisulfide, are also used by some producers. At least one producer (Nova Chemicals) is also marketing a controlled oxidation pretreatment which it claims provides significant reductions in coke buildup. Work is also underway at several national laboratories to develop ways of minimizing coking in hydrocarbon furnaces. Oak Ridge National Laboratory, for example, is working with the Materials Technology Institute and several chemical companies to develop aluminide-based materials for ethylene pyrolysis service.^{11,12,13}

All of these technologies are potentially interesting ways to enable ethylene producers to move toward increasingly severe—and increasingly productive—cracking conditions. Each of them, however, has limitations. The cast 35% Cr-45% Ni alloy has a solidus temperature even lower than the traditional HP45 Mod composition, shrinking the allowable process window between the service temperature and the melting temperature. Since localized melting—especially during decoking—will disrupt the protective surface oxide and aggravate coking, this alloy is likely to require increasingly tight process control. There is also concern that chromia-forming alloys such as the 35% Cr-45% Ni alloy may gradually lose their ability to reform a protective oxide scale after decoking and may begin to experience chromium volatilization at temperatures approaching 1200°C (2192°F). Wrought materials are very attractive as pyrolysis tubing materials because of their ability to be formed into long, small-diameter—and internally-profiled—tubes. Most can also be welded fairly readily. Unfortunately, current wrought alloys do not exhibit creep strengths comparable to their centrifugally-cast competitors. Coatings have advanced substantially in recent years, but cost and durability of these coatings remains a concern. Process modifications such as sulfur and steam injection are helpful, but reduce the overall efficiency of the process and may increase downstream disposal concerns.

3.3 Technology Improvements

It has been recognized for some time that oxide dispersion strengthened alloys have significant potential for use in ethylene pyrolysis furnaces and steam methane reformers. In 1995, Atkinson noted:

(Oxide dispersion strengthened alloys for use in ethylene pyrolysis and steam methane reforming) appear to be the alloys of the future. ...The Fe base (INCOLOY™ Alloy MA956) has a strength in excess of the best centricast alloys in its least favorable transverse direction. It also has excellent carburization and oxidation resistance. The Ni-base alloy (INCONEL™ Alloy MA 754) also has a very high strength and good oxidation resistance. Both would permit the raising of the gas outlet temperature to 1100°C compared with the current maximum of about 1040°C maximum using the strongest cast alloys. **There are, however, problems to be resolved relating to production and fabrication of these alloys before they can be considered to be serious contenders for this market.** (Bold added for emphasis.)⁸

Indeed, work has been underway in other parts of the world on using oxide dispersion strengthened alloys for ethylene pyrolysis service. A recent Japanese article, for example, discussed the use of Inconel® Alloy MA 754, an oxide dispersion strengthened nickel-base alloy, for use in radiant tubes.¹⁴ Similarly, a paper presented at the 13th Ethylene Forum in February 2001 described a cooperative effort between JGC Corporation of Japan and Special Metals Corporation to assess the potential for using Incoloy® Alloy MA956 as pyrolysis tubing.¹⁵ This work reported that Incoloy® Alloy MA956 had a creep strength more than twice that of current HP45 Mod pyrolysis alloys due to its oxide dispersion strengthening. Bench-scale coking/decoking tests also showed the alloy to exhibit a coking formation rate about one-half that of conventional 25%Cr-35% Ni pyrolysis tubing alloys.

This improved creep resistance and coking resistance makes Incoloy® MA956 particularly attractive as an alloy for ethylene pyrolysis tubing. The creep resistance is achieved by producing the material using mechanical alloying, a solid-state process which involves milling an elemental powder charge of the appropriate composition with fine (~20-40 nm) oxide particles to produce an oxide dispersion strengthened powder. The milled material is then consolidated by direct powder extrusion. After extrusion, the material is given a high-temperature anneal—typically 1300°C for 1 hr—to generate the coarse, elongated grains required for good high temperature strength.

The improved coking and carburization resistance of the alloy is presumably due to its high aluminum content and highly-stable duplex chromia/alumina surface oxide. Unfortunately, this high aluminum content also lowers ductility and fabricability, making the material challenging to use for radiant furnace coils. Cold forming of the material must be done at slightly elevated temperatures (~100°C) in order to minimize the likelihood of brittle fracture. More importantly, the material has limited weldability. It can be joined by fusion welding, but welded joints show both porosity and segregation of the oxide dispersoid. Accordingly, solid state joining techniques such as diffusion bonding and explosive welding are generally most successful. These techniques, however, are not well suited for either field fabrication or re-tubing of pyrolysis furnaces.

3.4 Program Objective

The work conducted under this program sought to overcome these limitations by creating a novel bimetallic pyrolysis tube having an inner core of Incoloy® MA956 surrounded by an outer sheath

of oxide dispersion strengthened Alloy 803. The Incoloy[®] MA956 provided improved coking resistance on the inner surface of the tube in contact with feedstock gases, and the ODS Alloy 803 provided improved fabricability. Oxide dispersion strengthening of the Alloy 803 provided the creep strength needed in the outer sheath in order to fully exploit the excellent creep strength of the Incoloy[®] MA956 core. To develop this novel tube, two key issues needed to be addressed: 1) development of the high-creep-strength ODS Alloy 803 alloy for the outer sheath and 2) development of a method for producing these bimetallic tubes from ODS powders.

Conventional Alloy 803 is currently marketed by Special Metals Corporation as a wrought alloy for use in small diameter ethylene pyrolysis tubes. The alloy has shown good resistance to the environment found on the fire side of radiant coils for ethylene production and excellent fusion weldability. Wrought Alloy 803, however, has much lower creep strength than Incoloy[®] MA956. At 1038°C, Alloy 803 exhibits a 1000-hr creep rupture strength of about 10 MPa.¹⁶ In contrast, Incoloy[®] MA956 exhibits a 1000-hr creep rupture strength of about 60 MPa at the same temperature.

Under the program, oxide dispersion strengthening was used to raise the creep strength of the Alloy 803. The resulting ODS Alloy 803 material was produced by mechanical alloying—the same process used to produce Incoloy[®] MA956. The principal challenge was optimizing the entire material processing sequence—starting alloy chemistry, dispersoid content, degree of milling and extrusion conditions—so that the material developed a coarse, elongated grain structure during the final recrystallization anneal. To achieve this, the material needed to exhibit a microstructure which pinned grain boundaries effectively during direct powder extrusion, yet allow these same boundaries to migrate during the final high-temperature anneal to produce secondary recrystallization.

The second key issue was development of a practice for fabricating the oxide dispersion strengthened bimetallic tubes. This practice had to be capable of producing tube exhibiting both uniform cladding thickness and good bonding between the ferritic MA956 and austenitic ODS Alloy 803. Since both ODS Alloy 803 and MA956 were produced as powders, the program focused on production of tube by direct powder co-extrusion. Special Metals currently produces Incoloy[®] MA956 tube by direct powder extrusion, and has used extrusion for commercial production of some non-oxide-dispersion-strengthened clad alloys. Direct powder co-extrusion, however, had not been previously used to produce bimetallic ODS tubes.

3.5 Program Structure

The program undertaken to address these two challenges involved four primary tasks:

- ODS Alloy 803 development,
- Bimetallic tube development,
- Material characterization, and
- Commercialization assessment.

The ODS Alloy 803 development involved two major activities:

- **Powder Processing.** This work involved developing an appropriate procedure for milling the Alloy 803 with fine yttrium oxide to obtain a uniform powder. Work was done using both prealloyed (atomized) and blended elemental Alloy 803 matrix material. Early in the program, however, it became apparent that using blended elemental powders had substantially more potential than using prealloyed powders. Accordingly most of the work under the program was done using blended elemental materials.
- **Extrusion and Recrystallization.** Once appropriate milling protocols were developed, the milled ODS Alloy 803 powder was canned, extruded and evaluated. Evaluations included microstructural characterization, mechanical testing and recrystallization tests.

The bimetallic tube development effort also involved two major thrusts:

- **Extrusion Process Modeling.** First, elevated temperature flow stress data was developed on the unrecrystallized ODS Alloy 803 and MA956 material. Using this flow stress data, the co-extrusion process was modeled using the DEFORM finite element metal forming simulation package marketed by Scientific Forming of Columbus OH. Since the tubes were radially symmetric, this simulation was done using a 2-D code.
- **Tube Fabrication.** Using the DEFORM simulation results as a guide, a series of Incoloy[®] MA956 / ODS Alloy 803 cans were fabricated and extruded to develop a suitable processing protocol for making the bimetallic tubes. These tubes were then evaluated using a combination of dimensional, microstructural and recrystallization studies.

The material testing work involved three major components:

- **ODS Alloy 803.** Preliminary screening studies were done on the ODS Alloy 803 produced under the program to assess ambient temperature tensile strength, elevated temperature oxidation resistance and stress rupture properties.
- **Joining Studies.** Arc welding studies were carried out on both sections of ODS Alloy 803 extrusions and bimetallic Incoloy[®] MA956 / ODS Alloy 803 tubes to assess their arc-weldability. These tests were done using manual gas tungsten arc (GTA) welding.
- **Coking Studies.** Laboratory-scale coking tests were conducted on Incoloy[®] MA956 sheet to confirm the improved coking resistance of this alloy compared to standard alloys such as Incoloy[®] 800. These tests were done using a thermogravimetric analysis (TGA) test rig created under the program. This rig provided real-time measurements of coupon weight gain as a function of time, data which has not been previously available in the literature.

The commercialization assessment work involved gathering information about two key areas:

- **Energy Savings.** Data was compiled from the literature to more accurately assess the potential energy savings to be realized from using bimetallic Incoloy[®] MA956 / ODS Alloy 803 tubes for production of ethylene.

- **User Requirements.** Information was compiled and documented from potential user organizations about requirements for successful implementation of bimetallic ODS pyrolysis tubes.

The results obtained from each of these efforts are contained in the following section.

4.0 Results and Discussion

The technical work performed under the program was conducted from October 1, 2002 through June 30, 2005. The findings obtained from the work are described below.

4.1 ODS Alloy 803 Development

As noted before, successful development of ODS superalloys requires optimization of both dispersoid content and prior upstream thermomechanical processing to insure that the material can be recrystallized successfully to the coarse-grained microstructure required for good elevated temperature properties. Dispersoids must be of the correct number, size and distribution to maintain a fine (< 1 micron) uniform grain size during powder consolidation and hot working, yet allow grain boundaries to migrate during the final anneal. Hot working operations must be sufficiently severe to provide a “susceptible” microstructure for recrystallization. Although prior technology and existing theoretical models provide some guidance, successful optimization generally requires a significant amount of empirical development. This program was no exception.

4.1.1 Powder Processing

The first portion of the program involved developing appropriate milling protocols for production of the ODS Alloy 803 powder. In order to expedite this work, a second, instrumented 1S attritor was installed at the Institute. A photograph of the unit is shown in Figure 2. It was configured for milling under a protective argon atmosphere and instrumented with a personal-computer-based data collection system. This data collection system could monitor and record the following milling parameters:

- Coolant inlet and outlet temperatures,
- Coolant flow rate,
- Milling chamber temperatures at 4 locations,
- Milling torque and rotational speed,
- Motor amperage, and
- Noise levels generated.

A schematic diagram of the monitoring system is shown in Figure 3. In addition, a watt-hour meter was installed on the power lines coming into the attritor so that energy requirements for mechanical alloying could be monitored during processing.

At the start of the program, a target composition was selected for the ODS Alloy 803 materials to be produced. This composition (in wt%) was: 25-26% Cr, 35-38% Ni, 0.5-1.0 Si, 0.5-1.0 Mn, 0.2-0.3 Al, 0.2-0.3 Ti, 10-40 ppm B, 0.15-0.25 Y_2O_3 and balance Fe. This composition is similar to that of wrought Alloy 803. The low level of Y_2O_3 was chosen primarily to maximize the fabricability of the alloy and to facilitate secondary recrystallization into the coarse-grained microstructure needed for good creep resistance.

Once the target composition was selected, milling studies were initiated. Trials were run on ODS Alloy 803 powders produced from both blended elemental and prealloyed charge materials. The blended elemental approach is relatively low cost and facilitates uniform dispersion of the yttria within each powder particle. Unfortunately, it also has potential for generating hard, incompletely-milled particles which may nucleate voids during deformation processing or elevated temperature service. Providing yttria particles can be dispersed appropriately, using prealloyed charge materials may reduce the number of void nuclei in the material, improving elevated temperature ductility and/or service performance. Accordingly, both approaches were evaluated under the program. To minimize contamination, all milling was done under a protective cover of argon gas.

First, a series of small-scale (~10 g) milling runs were performed in a Spex shaker mill to assess the general behavior of the Alloy 803 composition. Blended elemental charge materials milled quite well, readily producing fairly coarse, free-flowing powders without the addition of organic process agents. The prealloyed charge materials were more “gummy”, producing large, agglomerated particles. X-ray diffraction measurements showed both materials to undergo a substantial amount of mechanical deformation during processing. One lot of blended elemental ODS Alloy 803 powder was then milled in the 1S attritor using estimated milling parameters similar to those commonly used for Ni-based superalloys. The material also milled well in this machine, producing a free-flowing, slightly coarsened powder. This first heat of ODS Alloy 803 material was then canned and hot isostatically pressed into a cylindrical billet. Photographs of this billet in the HIP unit and after processing are shown in Figures 4 and 5.

Based on these initial milling results, a parametric study was undertaken to develop a more complete understanding of the milling behavior of the ODS Alloy 803 material and to identify optimum milling conditions. Work was carried out using both prealloyed and blended elemental charge materials. Prealloyed powders were milled in the 1S attritor for 24, 48, 72 and 96 hours at speeds of 70, 100 and 200 rpm. Blended elemental powders were milled in the same unit for similar times at speeds of 70, 100, 200 and 300 rpm. It was not possible to mill the prealloyed powders at 300 rpm due to excessive agglomeration. The resulting powders were characterized using a combination of screen analyses, optical metallography and microhardness measurements.

The powders obtained from the prealloyed and blended elemental starting materials were found to be quite different. The prealloyed powders appeared to be noticeably softer and more ductile than the blended elemental materials. Figures 6 and 7 show screen analyses obtained on both types of materials at each of the milling times examined. Both types of powders coarsened slightly with increasing milling time and coarsened markedly with increased milling speed. At both 100 and 200 rpm, the prealloyed powders were found to have a larger particle size than the prealloyed materials over the entire range of milling times investigated. Figures 8 through 14

Figure 2. IMP researcher loading 1-S attritor with an ODS Alloy 803 powder charge.

Figure 3. Block diagram of the data acquisition system on the 1-S attrition mill.

show the powder particle morphology observed in each material after 96 hours of milling. Note that a number of the prealloyed powder particles processed at the two higher speeds show cracks or voids. Similar features were not observed in the blended elemental materials.

Figure 15 shows the Vickers microhardness values observed on the milled powders. Note that the hardness data shown in the two graphs is identical; the only difference between them is that the top graph (Fig. A) shows the data plotted as a function of milling time, whereas the bottom graph (Fig. B) shows this data plotted as a function of total mill revolutions (i.e. mill speed x total milling time). Figure B allows one to separate out the competing effects of milling speed and milling time somewhat more easily. Both Figures A and B show that the blended elemental materials exhibited substantially higher hardness values than the prealloyed powders under equivalent milling conditions. This may be due to the voids present in the prealloyed materials or it may arise because the single-phase prealloyed powders exhibited less work hardening than the multi-phase blended elemental materials. The somewhat unusual behavior of the prealloyed powder milled at 200 rpm may not be significant, since both the 72 and 96-hr microhardness data showed large standard deviations (> 70 units). Figure B also suggests that the marked coarsening of the powders with increased milling speed is probably due primarily to increased milling energy at the higher speeds rather than to an increased number of collisions per unit time.

These milling studies showed that only the blended elemental powders could be processed successfully to the required high hardness level while maintaining the moderately-coarse particle size distribution required to facilitate powder handling. Furthermore, these blended elemental powders are likely to be substantially lower cost than prealloyed materials for large-scale, commercial production. Thus, the blended elemental materials exhibited much greater potential for large-scale production of high-quality ODS Alloy 803 material. Accordingly, all subsequent development work was done using blended elemental powders milled at a speed of 265 rpm in an oil-cooled 1S attritor. These conditions were chosen to insure that the milled powders exhibited little +60 mesh or -325 mesh material to maximize flowability and uniformity, saturation hardnesses greater than 600 H_v to provide uniform distribution of the yttria particles in the powder, and limited media contamination.

Figure 4. Hot isostatic press (HIP) located at the Institute of Materials Processing.

Figure 5. Can containing consolidated ODS Alloy 803 material after hot isostatic pressing.

Figure 6. Particle size distribution observed in prealloyed ODS Alloy 803 powders milled at various speeds and for various times.

Figure 7. Particle size distribution observed in blended elemental ODS Alloy 803 powders milled at various speeds and for various times.

4.1.2 Extrusion and Recrystallization Studies

Based on these Powder Processing studies, ODS Alloy 803 powders were produced by attrition milling blended elemental powders under argon in the Union Process 1S attritor for up to 96 hours. The powders were then charged into mild steel cans, hot-outgassed at $\sim 400^{\circ}\text{C}$, and sealed. The evacuated cans were then extruded into 19 mm (0.75 in) rounds (extrusion ratio = 16:1) on a 6.7 MN (750T) press at Special Metals Corporation in Huntington, WV. Each extrusion was ~ 2 m long with a mass of ~ 6 kg.

Generation 1 powders, the first materials produced under the program, were milled for 48 hrs and then extruded at two temperatures— 1050°C and 1100°C .

The extruded bars were then given recrystallization anneals in air at 1300°C and evaluated by optical metallography. Both materials contained residual, partially-milled particles of Cr and showed evidence of partial secondary recrystallization in some areas. The 1050°C extrusion showed slightly more recrystallized material, so the lower extrusion temperature was adopted for all remaining extrusions produced under the program. The mixed structure observed in this Generation 1 material was attributed primarily to a non-uniform distribution of the yttria dispersoid.

Generation 2 powders were then produced using finer Cr starting powders and an alternative technique for pre-blending the yttria dispersoid with the metallic charge. Milling time was also increased from 48 to 96 hrs and yttria content of the material was raised from 0.2 wt% to 0.3 wt%. The milled powder was extruded into a 19 mm round at 1050°C , annealed at 1300°C and evaluated by optical microscopy. This material showed a noticeably more uniform microstructure than the Generation 1 alloy and contained less very-fine-grained material after the

Figure 8. Optical micrograph of ODS Alloy 803 prealloyed powder 1-S attrition-milled for 96 hours at 70 rpm. Etched with HCl + HNO₃.

Figure 9. Optical micrograph of ODS Alloy 803 prealloyed powder 1-S attrition-milled for 96 hours at 100 rpm. Etched with HCl + HNO₃.

Figure 10. Optical micrograph of ODS Alloy 803 prealloyed powder 1-S attrition-milled for 96 hours at 200 rpm. Etched with HCl + HNO₃.

Figure 11. Optical micrograph of ODS Alloy 803 elemental powder 1-S attrition-milled for 96 hours at 70 rpm. Etched with HCl +HNO₃.

Figure 12. Optical micrograph of ODS Alloy 803 elemental powder 1-S attrition-milled for 96 hours at 100 rpm. Etched with HCl +HNO₃.

Figure 13. Optical micrograph of ODS Alloy 803 elemental powder 1-S attrition-milled for 96 hours at 200 rpm. Etched with HCl +HNO₃.

Figure 14. Optical micrograph of ODS Alloy 803 elemental powder 1-S attrition-milled for 96 hours at 300 rpm. Etched with HCl +HNO₃.

Figure A

Figure B

Figure 15. Effect of charge material and milling speed on the microhardness of milled ODS Alloy 803 powders. Figure A—Microhardness as a function of milling time. Figure B—Microhardness as a function of mill revolutions.

recrystallization anneal. Nevertheless, the average grain size was still far short of that required for good elevated temperature performance. Scanning electron microscopy and electron microprobe evaluations showed fairly uniform Y contents in most regions, but also showed occasional large ($\sim 5 \mu$) Y-rich particles along grain boundaries. This raised concerns about the quality and size distribution of the yttrium oxide powders used for the Generation I and Generation 2 materials. Accordingly, new nanometer-sized yttrium oxide was obtained and analyzed to verify that its particle size was, in fact, approximately 35 nm.

Generation 3 materials were then produced using 0.4 wt% of this new yttrium oxide, as well as finer Ni and Fe elemental powders. Like Generation 2, the material was milled for 96 hrs, extruded into a 19 mm bar, recrystallized at 1300°C and evaluated. After recrystallization, the bar exhibited both larger and more uniform grains than previous alloys. Field emission scanning electron microscopy confirmed that the yttria dispersoids were fairly uniformly distributed. Ambient temperature tensile testing of the recrystallized material showed a tensile strength of 725 MPa (105 ksi) with an elongation of 15%. For comparison, commercial Incoloy[®] MA956 exhibits a room temperature tensile strength of 650 MPa with about 12% elongation. This Generation 3 material showed a clear improvement over earlier alloys, but still fell short of the microstructure required for optimum high temperature creep resistance.

Generation 4 powders were then produced using the same milling practices as for Generation 3, except that the yttria level was increased to 0.5 wt%. An organic process agent (0.1 wt %) was also added to control material buildup in the attritor during milling. Like previous materials, this Generation 4 material was extruded into a 19 mm bar, annealed at 1300°C and evaluated by optical microscopy. It showed markedly-better recrystallization response than previous alloys. Material taken from the middle of the extrusion showed 80 to 85% very coarse-grained material, with the remainder of the microstructure showing a grain size similar to that of previous alloys. The grain aspect ratio in coarse-grained regions ranged from 2.5:1 to 9.4:1, with an average value of 4.0:1. Figure 16 shows a comparison of the recrystallized microstructures observed in the Generation 1, 3 and 4 alloys. Material from the head and tail of the extrusion showed somewhat more fine-grained material.

Figure 16. Grain structure observed in Generations 1 (left), 3 (center) and 4 (right) of ODS Alloy 803 material. Note the clear increase in grain size as processing was optimized

The recrystallized Generation 4 materials, however, also showed a precipitate phase not observed in previous alloys. In the coarse-grained regions, these second-phase particles occurred primarily along grain boundaries; in the finer-grained regions, they occurred as both intergranular and intragranular particles. Energy-dispersive x-ray analysis and x-ray diffraction showed the particles to be Cr_{23}C_6 carbides. As shown in Table 2, chemical analysis confirmed that the carbon level of this Generation 4 material was higher than expected. Ambient temperature tensile testing showed the recrystallized material to have a tensile strength of 985 MPa (143 ksi) with 16% reduction in area. It was not possible to obtain yield or elongation data on the bars due to experimental difficulties with the extensometer. For comparison, cold rolled Incoloy[®] MA956 sheet exhibits a tensile strength of about 95 ksi (650 MPa).

Table 2. Chemical Analysis of Generation 4 Materials (Wt. %)

Element	Actual	Target
Ni	36.54	37
Fe	37.04	36
Cr	23.21	26
Al	0.23	0.3
Ti	0.23	0.3
Mn	0.66	0.8
Si	0.66	0.8
Y*	0.3	0.4
C	0.25	0.08

*Present as Y_2O_3

These results show that coarse, elongated grain structures can be obtained in extruded ODS Fe-Ni-Cr alloys. Current commercial ODS alloys are based on either the Fe-Cr or Ni-Cr system, and prior anecdotal evidence had suggested that ODS Fe-Ni-Cr alloys might be significantly more difficult to recrystallize than their Fe-Cr and Ni-Cr counterparts. This work opens the possibility for using ternary Fe-Ni-Cr compositions to produce lower-cost ODS alloys.

4.2 Tube Simulation

Work was also undertaken to model direct powder extrusion of bimetallic tubes using finite element techniques. Modeling was done using DEFORM, a large-scale plastic deformation code marketed by Scientific Forming.[†] The work involved developing appropriate flow stress data for both ODS Alloy 803 and Incoloy[®] MA956, simulating extrusion of a solid ODS Alloy 803 rod to verify modeling techniques, and then extending this work to direct powder extrusion of bimetallic tubes.

4.2.1 Flow Stress

As-extruded (unrecrystallized) Incoloy[®] MA956 and ODS Alloy 803 (Generation 1) bar was machined into cylindrical coupons 14.5 mm high x 10 mm dia. These coupons were then subjected to constant strain rate uniaxial hot compression testing to a true strain of at least 0.5 at Dynamic Systems, Inc.[‡] Testing was done at three temperatures (950°C, 1050°C and 1150°C) and three strain rates (0.04/s, 1/s and 25/s). The resulting data were corrected for adiabatic heating using standard techniques.¹⁷ Multiple regression was then used to fit this flow stress data to an expression of the form:

[†] Scientific Forming Technologies Corporation, 5038 Reed Road, Columbus, Ohio 43220-2514.

[‡] Dynamic Systems Inc., 323 Route 355, Poestenkill NY, 12140.

$$\sigma = A'(\dot{\epsilon})^m \exp\left(\frac{mQ}{RT}\right)$$

where σ is the observed flow stress at a true strain of 0.5, $\dot{\epsilon}$ is strain rate, m is strain rate sensitivity, Q is the apparent activation energy for plastic deformation, and RT has its usual meaning. These results were then used to calculate the Zener-Holloman parameter:

$$Z = \dot{\epsilon} \exp\left(\frac{Q}{RT}\right)$$

for each data point.¹⁸ Finally, the flow stress data was plotted as a function of this Zener-Holloman parameter.

The results obtained for both the Incoloy[®] MA956 and ODS Alloy 803 are shown in Figure 17. Note that the large difference in the Zener-Holloman parameter for the two materials is due to the large difference in Q observed for the two alloys. The two lines represent extensions of the measured flow stress data to cover the temperatures and strain rates needed for the finite element simulations.

At high temperatures and low strain rates, the flow stresses of the two materials were comparable; under more severe deformation conditions, the flow stress of the ODS Alloy 803 was somewhat higher.

When necessary, data was extrapolated to compressive strains greater than 0.5 by assuming that flow stress was independent of strain for true strains ≥ 0.5 .[§]

4.2.2 DEFORM Modeling

DEFORM does not have capabilities for modeling consolidation of loose powders. Accordingly, powder extrusion was modeled by assuming that the powders being processed behaved as porous solids.¹⁹ Using this model, the powder column of the extrusion billet consistently consolidated to full density before any material broke through the die opening. Accordingly, the results obtained should be reasonably representative of ODS material flow during extrusion, even though the porous material model cannot effectively represent powder behavior during the early stages of powder densification.

Figure 17. Flow stress observed in as-extruded Incoloy[®] MA956 and ODS Alloy 803 as a function of the Zener-Holloman parameter.

[§] This is a rather crude approximation for some of the temperature/strain rate conditions evaluated. Nevertheless, it appeared to be of sufficient accuracy to provide useful results for the extrusion conditions simulated.

Model geometry and process parameters were based on the hardware and process conditions used for extrusion on the press at Special Metals. For simplicity, the metal can surrounding the powder billet was neglected for most simulations. To minimize the computational difficulties involved in modeling multiple deforming bodies (e.g. material penetration, interfacial separation and “triple points” where three deformable bodies touch), extruded material was trimmed periodically throughout the simulation. After trimming, the unextruded portion of the billet was remeshed. This maintained a majority of the finite elements in the deforming billet rather than in the extrudate. Initial simulations were run on a Unix-based Sun workstation, but later work was done on a PC-based system. The PC code was found to be more robust for the types of computations being performed.

Extrusion of 19 mm diameter rounds was simulated first to verify the modeling protocol. The Generation 3 material was extruded at a nominal temperature of 1037°C. Allowing for adiabatic heating, the actual extrusion temperature was estimated to be ~1137°C. A comparison of actual extrusion pressure for this Generation 3 material with predicted extrusion pressure for ODS Alloy 803 extruded isothermally at 1137°C is shown in Figure 18. Note that the two curves agree quite well. The deviation between measured and predicted pressure at the beginning of extrusion undoubtedly reflects the use of DEFORM’s porous material model to simulate powder compaction. These results provided confidence that finite element analysis could provide useful information about both the deformation of extrusion cans and the flow characteristics of ODS alloys during extrusion of bimetallic tubes.

4.3 Tube Fabrication

Direct powder extrusion of conventional tubes is usually done by fabricating a tubular can from two concentric tubes—an inside tube with an inner diameter just large enough to slide over the mandrel of the extrusion press and an outside tube with an outer diameter slightly smaller than the extrusion container. Cylindrical caps on the top and bottom of the can maintain the alignment of these two tubes and enclose the column of powder to be converted into tube. The tubular can is extruded over a mandrel having a diameter equal to the inside diameter of the final tube. To fabricate bimetallic Incoloy® MA956 / ODS Alloy 803 tubes, one has two options. First, one can fabricate the tubular can using an inner thick-walled tube of Incoloy® MA956 and fill the annular space between the inner and outer tubes with ODS Alloy 803 powder. For this “tube/powder” case, the outer tube is a sacrificial material such as steel that is removed after extrusion. Alternatively, one can fabricate the tubular can using sacrificial material for both the inner and outer tubes. In this “powder/powder” case, the annular space between the two tubes is filled with concentric rings of the two powders being used for the bimetallic tube.

Figure 18. Comparison of predicted and observed pressure for extrusion of 19 mm dia. bars of ODS Alloy 803

4.3.1 Tube/Powder Extrusion

At the start of the program, it was envisioned that the bimetallic tubes to be produced would have a thin core of Incoloy[®] MA956 surrounded by a much thicker outer sheath of ODS Alloy 803. This geometry minimizes concerns about the low ductility and field fabricability of Incoloy[®] MA956, as well as lowers the cost of the Incoloy[®] MA956 tube required for the final product. Accordingly, first-generation clad tube was produced using the tube/powder approach. About 5 kg of ODS Alloy 803 powder was canned in a mild steel can containing a central tube of unrecrystallized Incoloy[®] MA956. This can was extruded at an extrusion ratio of 6:1 into a 12 mm ID x 39 mm OD tube with a 0.5 mm layer of Incoloy[®] MA956.

This extrusion was not particularly successful. Despite the low extrusion ratio, the tubular can ruptured near the front of the extrusion. Clad tube was obtained from the middle and tail portions of the extrudate, but the outer layer of ODS Alloy 803 powder did not consolidate to full density. The Incoloy[®] MA956 core varied in thickness from point to point and cracked slightly in several locations. Recrystallization trials performed on coupons cut from the outer ODS Alloy 803 matrix sheath showed that this material recrystallized heterogeneously like other Generation 1 materials.

At first, the fracture of this initial tubular extrusion can was puzzling. Finite element modeling of the tube/powder process, however, provided a clear explanation. If the outer diameter of the solid Incoloy[®] MA956 tube is either very small or very large relative to the outer diameter of the billet and the extruded tube, the tube/powder approach can work well. Otherwise, the central, fully-dense Incoloy[®] MA956 tube will be pushed into—or through—the endcap on the nose of the billet while the ODS Alloy 803 powder is being compacted. Even if the endcap does not rupture, the resulting nonuniform deformation will lower the yield of acceptable tubing from the billet. The modeling work showed that placing a thick steel plate on the nose of the extrusion billet could ameliorate the situation, but would not cure it.

4.3.2 Powder/Powder Extrusion

As the program evolved, it became clear that potential users of the bimetallic pyrolysis tube being developed would prefer having a relatively thick layer of Incoloy[®] MA956 on the inside of the tube to assure long-term service performance. After characterizing the initial tube extrusion, reviewing the modeling work, and prototyping several tubular can designs, Michigan Tech and Special Metals decided that future bimetallic tubes should be fabricated from powder/powder rather than tube/powder billets. The powder/powder approach both avoids the need for Incoloy[®] MA956 / mild steel welds during can fabrication and minimizes the chance of can failure during extrusion.

Accordingly, extrusion of a powder/powder billet with an inner core of Incoloy[®] MA956 powder and an outer sheath of ODS Alloy 803 powder was simulated using DEFORM. The billet was modeled using 750 to 1500 elements in each of the two deforming powder columns, and it was possible to simulate isothermal extrusion of a 300 mm billet down to a residual extrusion butt of about 50 mm. Depending on the number of elements in the model, the extrudate generally needed to be trimmed from one to three times. Runs required one to three days on a 1 GHz PC. Initial runs were done as isothermal simulations, but the final run was done as a full non-isothermal simulation. In each case, the first material to exit the die was almost entirely Incoloy[®] MA956. After this initial transient, the radial position of the Incoloy[®] MA956/ODS

Alloy 803 interface agreed fairly well with what one would predict by assuming equal deformation of the two powder alloys. The position of this interface did, however, shift slightly with increasing ram travel.

Figure 19 shows the temperature distribution observed in the powder billet during quasi-steady state extrusion after the initial startup transient. The curved dark line running through the mid-thickness of the billet represents the boundary between the inner Incoloy[®] MA956 and the outer ODS Alloy 803. Note that the ODS Alloy 803 in the outer, highly-strained region of the billet exhibits a maximum temperature on the order of 1150°C, whereas the inner, less-highly strained Incoloy[®] MA956 near the inside diameter of the tube shows a temperature of about 1000°C. Figure 20 shows the maximum strain observed on the inside

Figure 19. Temperature distribution observed during simulated non-isothermal extrusion of a bimetallic tube.

(blue) and outside (red) of the bimetallic tube as the tube exits the die.^{**} After the initial startup transient, the maximum strain on the inside surface of the tube is on the order of 3.0. The maximum strain on the outside surface is somewhat higher, ranging from about 4.5 to 5.5 as the tube is extruded. Figure 21

Figure 20. Maximum strain observed on the inside (blue) and outside (red) surfaces of the bimetallic tube as a function of extrusion time (i.e. ram travel) during simulated non-isothermal extrusion.

shows a representative strain rate profile observed in the billet after the initial transient. Near the inside diameter of the tube, maximum strain rates are on the order of 60/s. At the outside surface of the tube, strain rates are substantially higher—on the order of 150/s. These variations in temperature, strain and strain rate through the thickness of the tube are important because they are likely to impact the recrystallization behavior of each alloy in the final extruded bimetallic tube.

^{**} The horizontal axis of this graph is actually plotted as time rather than distance since time was used as the independent variable for all DEFORM simulations. Since the ram traveled at a constant rate, however, ram travel is directly related to extrusion time.

This finite element modeling demonstrated that the powder/powder approach had good potential for producing suitable bimetallic tubes. Two attempts were then made to produce actual bimetallic tubes using this approach. First, a tubular extrusion can was fabricated using two concentric mild steel tubes connected by endcaps. This can was then filled with an inner ring of Incoloy[®] MA956 powder nominally 17 mm thick and an outer ring of ODS Alloy 803 powder nominally 13 mm thick. These thicknesses were chosen so that the extruded Incoloy[®] MA956 and ODS Alloy 803 layers would be nearly equal in thickness. The billet was then extruded into a 32 mm OD x 16 mm ID tube at Special Metals. It extruded successfully, exhibiting only minor surface cracking near the front of the extrusion. After extrusion, this tube was intended to be acid-leached to remove the inner and outer steel can. Unfortunately, the tube was leached incorrectly and showed substantial cracking when it was removed from the leach tank. It was a total loss.

Figure 22. Bimetallic 32mm OD x 16mm ID tube produced by direct powder extrusion. Inner core (light) is Incoloy[®] MA956. Outer case (dark) is ODS Alloy 803. The steel can is also visible on the inside and outside diameters.

Figure 21. Representative strain rates (sec^{-1}) observed at quasi-steady state during simulated non-isothermal extrusion of bimetallic tube.

Characterization of remnant pieces, however, showed that the extruded tube did have the desired bimetallic geometry, although the thickness of the inner Incoloy[®] MA956 layer varied slightly around the circumference. Some intermixing of the Incoloy[®] MA956 and ODS Alloy 803 powders also occurred in a few locations.

This powder/powder billet was then remade and re-extruded at Special Metals. The first portion of the billet extruded successfully, but then the mandrel on the extrusion press stuck and fractured, forcing the remainder of the billet to be scrapped.^{††} A photograph of material from the front of the extrusion is shown in Figure 22. The inner core of Incoloy[®] MA956 and outer sheath of ODS Alloy 803 are clearly visible, as is the thin steel can on both the inside and outside diameters. The interface between the Incoloy[®] MA956 and ODS Alloy 803 was generally sharp, although some intermixing was seen in a few locations. No cracking was observed. After annealing at 1300°C for 1 hr, the outer ODS Alloy 803 recrystallized to a coarse-grained microstructure, but the

^{††} Unfortunately, it was not possible to remake this billet a second time due to contractual issues.

inner Incoloy® MA956 remained fine-grained. This lack of recrystallization in the core is hardly surprising, since the ram speed of the extrusion press decreased markedly as the mandrel began to stick. The inner, less highly strained material probably did not experience the critical extrusion strain rate needed to initiate secondary recrystallization.

These results clearly demonstrate that direct powder co-extrusion using a powder/powder tubular billet has good potential for producing bimetallic pyrolysis tubes. Additional work, however, is needed to more fully develop the approach. The manual technique used for filling the powder can under this program was labor-intensive and required careful attention to detail. Development of an improved method for filling cans, perhaps even an automated system, would be desirable. Additional work on extrusion process development is also needed. The mandrel fracture observed on the second bimetallic extrusion needs to be more fully explored, as does recrystallization of the inner Incoloy® MA956 core. This can be done most effectively using a combination of non-isothermal finite element simulation and tubular extrusions.

4.4 Tube Testing

Preliminary oxidation and stress rupture screening tests were conducted on the extruded bars of ODS Alloy 803 and joining studies were conducted on the extruded bimetallic tubes. Laboratory coking studies were also conducted on the Incoloy® MA956 material to verify the improved coking resistance of this alumina-forming alloy.

4.4.1 Oxidation and Stress Rupture

Oxidation testing of the ODS Alloy 803 was done by measuring the weight gain of test coupons exposed to laboratory air at 1000°C for times up to 840 hrs. Machined coupons of as-extruded (unrecrystallized) ODS Alloy 803 and unrecrystallized bimetallic Incoloy® MA956 / ODS Alloy 803 tube from the final powder/powder extrusion were placed in an electrically-heated furnace. To collect data, the coupons were carefully removed from the furnace, cooled, weighed, and then returned to the furnace for additional elevated temperature exposure. As-extruded materials were used to minimize differences due to the varying recrystallization response of the alloys.

Figure 23. Oxidation of ODS alloys in laboratory air at 1000°C as a function of time.

The results obtained are shown in Figure 23. Both materials exhibited a slight weight gain during the first 168 hrs (7 days) of exposure, and a small amount of visible scaling during the first 336 hrs (14 days). After that, however, the mass of the coupons was nearly independent of time.

The stress rupture testing was conducted at Special Metals Corporation as an in-kind contribution to the program. Six stress rupture blanks were cut from the center of the Generation 4 ODS Alloy extrusion, recrystallized at 1300°C for 3 hours, air cooled and then machined into standard cylindrical stress rupture bars. These bars are currently being tested at Special

Metals. Three bars are being tested at 982°C (1800°F) and 56 MPa. The remaining three bars are being tested at 1093°C (2000°F) and 27 MPa. A typical cast HP modified microalloy (Paralloy HW39M) exhibits a stress rupture life of 100 hours under these conditions.

4.4.2 Joining Studies

Gas tungsten arc (GTA) welding trials were also conducted on the extruded ODS Alloy 803 materials. At the start of the program, it was expected that bimetallic Incoloy[®] MA956 / ODS Alloy 803 tubes would exhibit substantially better weldability than monolithic Incoloy[®] MA956. Wrought Alloy 803 is recognized as a readily-weldable material. In the bimetallic tube, it was expected that the Alloy 803 contained in the outer sheath would provide enough dilution of the Incoloy[®] Alloy MA956 core to produce a sound joint.^{††}

Initial welding trials were done by making manual GTA bead-on-plate (actually bead-on-round) welds on extruded ODS Alloy 803 bars. Beads were made using both Inconel[®] Alloy 82 and Inconel[®] Alloy 617 filler materials, the two materials most commonly recommended as filler alloys for ODS alloys. Metallography of the welds made with either filler metal showed a significant amount of dispersoid aggregation and porosity, particularly near the fusion line. A typical microstructure is shown in Figure 24. Both the aggregation and porosity are recognized concerns for fusion welding of ODS alloys, although the extent of porosity observed was somewhat greater than anticipated.

Manual GTA welds were then made on the extruded Incoloy[®] MA956 / ODS Alloy bimetallic tube. Welds were made with both filler materials using prepared joints having a 45° bevel (90° included angle). The best results were obtained using Type 82 filler metal, although all joints produced showed some degree of oxide agglomeration and porosity. Scanning electron microscopy of various coupons also showed that the oxide dispersoids tended to segregate to the surface of the voids, further degrading the quality of the dispersoid distribution. These results strongly suggest that the limited weldability of current-generation ODS materials is associated more with the mechanical alloying process used to produce the materials than with the matrix chemistry of the alloy.

These findings spawned additional work to explore alternative approaches for improving the weldability of ODS Alloy 803 and similar materials. One

Figure 24. GTA fusion zone between ODS Alloy 803 and Inconel[®] 617 filler metal. Note porosity and aggregation of oxides.

^{††} Note that this initial thinking was based on the program's initial assumption of a thin Incoloy[®] MA956 core surrounded by a much thicker ODS Alloy 803 sheath.

problem with current ODS materials is that the nano-sized yttrium oxide particles used as a dispersoid have a density significantly lower than that of the matrix alloy, causing them to segregate to the top of a melt. Using other, higher-density materials such as samarium or neodymium oxide as a dispersoid has excellent potential for minimizing this segregation. The porosity observed in the welded ODS alloys probably arises from gases entrapped in the matrix powders during milling. One may be able to overcome this by dispersing some sort of dispersoid “concentrate” into a molten alloy. Several attempts were made to produce an oxide dispersion strengthened variant of Alloy 803 using commercial nanometer-sized neodymium oxide as a dispersoid and melt-based processing. An invention disclosure was also filed with Michigan Technological University outlining this approach. Significant additional work, however, is likely to be required to develop this approach into a commercially-viable product.

4.4.3 Coking Studies

Coking studies were also done under the program to confirm the anticipated reduced coking rate of the Incoloy® MA956 material. This work involved assessing the rate of coke deposition in a flowing hydrocarbon/steam mixture using a custom-built thermogravimetric system. Dr. Lyle Albright of Purdue University assisted with these coking studies. A schematic of the coking test rig constructed is shown in Figure 25. The system is essentially a vertical thermogravimetric

Figure 25. Schematic of the coking test rig at Michigan Technological University.

analysis (TGA) system with an associated hydrocarbon gas train. Coking test coupons were suspended from a Cahn microbalance in a 50-mm OD, 3-zone quartz tube furnace.^{§§} Hydrocarbon gas flowed through a preheater/mixer and heated water-filled bubbler and then into the bottom of the tube furnace. The bubbler supplied the water vapor needed to provide a hydrocarbon/steam mixture to the vertical furnace. Testing was done using N-butane and nominally 50% steam at a total room-temperature gas flow rate of 0.03 l/s. Most coking tests were conducted at a nominal temperature of 800°C using coupons 19 mm wide. Exit gases were flamed off under a fume hood. Normal butane was used as the hydrocarbon feedstock because the coking characteristics of this gas are similar to those of ethane, and high purity ethane was not readily available from Michigan Tech's compressed gas supplier. A photo of the test system is shown in Figure 26.

Figure 26. The coking test rig at Michigan Technological University.

Comparative coking tests were run on Incoloy[®] MA956 and a baseline Incoloy[®] 800 sheet. The compositions of these two materials are shown in Table 3. The Incoloy[®] MA956 sheet was prepared by manually abrading on 120 grit abrasive paper and then pre-oxidizing in air at 1100°C for 30 minutes. The Incoloy[®] Alloy 800 sheet was also prepared by manually abrading on 120 grit paper. It was then tested in two conditions—as-abraded (with no intentional oxidation pretreatment) and after pre-oxidizing in air at 1100°C for 30 minutes (the same treatment as used for the Incoloy[®] MA956.). The test procedure involved:

- Preparing the test coupons (up to three per run) and mounting them in the furnace,
- Preheating the furnace to 800°C using an argon purge gas and holding at this temperature for an extended period (typically overnight) to allow thermal transients to stabilize,
- Replacing the argon purge gas with the N-butane/steam mixture and allowing this hydrocarbon/steam mixture to flow past the coupons for 7 hrs. The temperature in the region of the coking sample was estimated to be 790°C, and the gas flow velocity in this region was estimated to be 62 mm/s.
- Shutting off the N-butane/steam mixture, restarting the argon purge gas, purging the system overnight, and then allowing the furnace to cool slowly.

The extent of coking was assessed primarily by measuring the increase in the mass of the coupon during hydrocarbon exposure. Up to three coupons could be included in each furnace run—a center (75 mm long) TGA coupon connected to the Cahn microbalance for collection of mass change data in real time, and two shorter (25 mm long) coupons on either side of this central

^{§§} Currently marketed through Thermo Electron Corporation—Materials Characterization group, located in Newington, NH, 03801, USA.

coupon. Coking of the two side coupons was monitored by pre- and post-exposure weighings on a separate, stand-alone analytical balance.

Data obtained from representative coking runs is summarized in Figures 27 and 28. Mass vs. time traces observed on TGA coupons of each material are shown in Figure 27. These data were obtained at a nominal temperature of 790°C using a mixture of 50% N-butane and 50% steam at a flow rate of 2 L/min. The system was purged with flowing argon both before and after butane addition. The oxidized Alloy 800 coupon (blue) was abraded to a 120 grit finish and then oxidized in air at 1100°C for 30 minutes prior to testing. The unoxidized Alloy 800 coupon (purple) was abraded to a 120 grit finish with no subsequent oxidation treatment prior to testing. The Incoloy® MA956 coupon (red) was abraded to a 120 grit finish and then oxidized at 1100°C for 30 minutes prior to testing.

Table 3. Chemical Composition of Materials Used for Coking Tests (Wt. %)

Element	Incoloy® MA956*	Incoloy® 800†
Ni	0.12	33.
Fe	Balance	Balance
Cr	19.75	22.
Al	4.70	0.40
Ti	0.37	0.40
Mn	0.12	1.5 max
Si	0.10	1.0 max
Y‡	0.42	NA
C	0.021	0.10 max

*Heat analysis of material tested

†Nominal chemistry

‡Present as Y₂O₃

This observed mass gain represents coking on both the test coupon and the supporting wire. Baseline coking runs of the TGA system done with no test sample, however, showed that the mass of the supporting wire increased linearly with time during the 7-hr exposure period. By subtracting the mass gain of the wire during each run (~10-12 mg), it was possible to determine the mass gain of just the coupon and to compare this value with the mass change results obtained from pre- and post-exposure weighings of these same coupons. The results obtained are shown in Figure 28. The two sets of data generally agree quite well, although the TGA results show somewhat lower coking rates for the Incoloy® 800 sheet. This is not surprising, since the Incoloy® 800 sheet showed larger mass gains during both the initial and final stabilization holds, probably due to greater oxidation of the Incoloy® 800 sheet during these periods.

Figures 29 through 33 show coke deposits which formed on the various coupons. Figures 29 through 31 show optical macrographs of the 25 mm and 75 mm coupons from each run. The pre-oxidized 25 mm long Incoloy® 800 coupons clearly showed substantially heavier deposits than any of the other materials. These deposits were also “fluffier” and much less adherent than those observed on the other materials. The as-abraded Incoloy® 800 and Incoloy® MA956 exhibited denser and more uniform surface coatings of coke. Both the as-abraded Incoloy® 800 and Incoloy® MA956 did show some non-uniformities in surface discoloration, but there were no consistent patterns between the various materials.

Figure 32 shows polished, unetched cross-sections of the three materials. All were prepared from the 25 mm coupons. The oxidized Incoloy® Alloy 800 clearly shows substantially more surface damage than the other two materials, although this degradation undoubtedly represents a mixture of oxidation and coke deposition. Note that essentially no surface degradation is visible on the Incoloy® MA956 material after testing. Figure 33 shows scanning electron microscopy images of the coke deposits observed on the Incoloy® MA956 sheet after a coking run. As

Figure 27. Mass vs. time traces observed on TGA coupons of oxidized Alloy 800 (blue), unoxidized Alloy 800 (purple) and Incoloy® MA956 (red) obtained using the Michigan Tech coking test rig.

shown in the left micrograph, the largest coke deposits formed adjacent to edges on the coupon, although smaller deposits were fairly uniformly distributed across the surface of the material. Observation at higher magnification clearly showed that the deposits consisted almost entirely of globular coke.

These findings provide new information in several areas. Most published coking rate data on coupons has been obtained using horizontal furnaces. The test rig developed under the program enables one to collect coking data on information on coupons mounted in a vertical furnace. This vertical orientation more closely simulates the behavior of the vertical coils found in a commercial ethylene pyrolysis furnace. The system also provides information about how the rate of coking varies with radial position and mode of attachment (i.e. stiff or flexible wire). These effects have generally not been considered in horizontal furnaces. In addition, the test rig provides—for the first time—real-time data about the rate of coke deposition on substrates. Previous test systems could provide only pre- and post-exposure results. Though not explored under this program, this real-time monitoring capability may also be very valuable for studying the kinetics of decoking reactions.

The results also provided new information about the coking resistance of the materials evaluated. It is generally agreed that coke deposits form on metallic surfaces through three principal mechanisms.^{20,21} Filamentous coke forms through metal or metal carbide catalyzed reactions on the surface of the material. Globular coke particles form through impingement of tar droplets from the gas phase onto the surface of the sheet. Finally, both filamentous and globular coke particles can grow through solid/gas reactions with free radicals or unsaturated hydrocarbons.

The globular particles observed on the Incoloy[®] MA956 sheet indicates that most of this coke formed through deposition—and possibly growth—of tar droplets. Accordingly, the mixed chromia-alumina scale formed on the sheet did confer effective resistance to filamentous coke formation. Coke deposition through impingement of tar droplets would also explain why the rate of coke deposition varied significantly with radial position in the furnace, was greatest near the edges of the coupon and increased on coupons which swung freely in the gas stream.

Figure 28. Coking Behavior of Incoloy[®] MA956 and Incoloy[®] 800 Sheet. Graph shows a comparison of coke deposition rates on 76 mm long coupons as measured by pre- and post-exposure weights and by the real-time thermogravimetric data.

The program results also clearly confirmed the improved coking resistance of Incoloy[®] MA956 relative to conventional chromia-forming Fe-Ni-Cr alloys such as Incoloy[®] Alloy 800. In the tests performed, the preoxidized Incoloy[®] MA956 showed more than a factor of 3 reduction in coke formation compared to Incoloy[®] 800. The TGA data also showed the interesting—and unanticipated—result that the rate of coke deposition on the coupons was independent of time over the 7-hour time interval studied. It would be valuable to know if similar behavior is observed under other coke deposition conditions, such as at longer times, at higher temperature and/or with different feedstock gases.

Figure 29. Oxidized Incoloy 800[®] coupons after coking trial. A—Front side. B—Back side

Figure 30. Unoxidized Incoloy 800[®] coupons after coking trial. A—Front side. B—Back side.

Figure 31. Incoloy[®] MA956 coupons after coking trials. A—Front side. B—Back side.

Figure 32. Microstructures observed on polished cross-sections of oxidized Incoloy[®] Alloy 800 (A), unoxidized Incoloy[®] Alloy 800 (B) and Incoloy[®] MA956 (C) after coke testing.

Figure 33. Scanning electron microscope images of the coke deposits observed on a 25 mm coupon of Incoloy[®] MA956 after a coking test run.

4.5 Commercialization and Economic Considerations

The bimetallic tube technology explored under this program has potential for domestic energy savings of up to 4.1 trillion BTU/year (4.3×10^{15} J/year) and a reduction of 370,000 tons (340,000 tonnes) of CO₂ emissions in short-residence-time furnaces. This represents an energy savings and CO₂ emissions reduction of about 3.3%. Over the long term, the technology is also applicable to other types of ethylene pyrolysis furnaces. If applied to these other types of furnaces, the technology has potential for increasing these domestic energy savings of 4.1 trillion BTU/yr (4.3×10^{15} J/year) and CO₂ emission reductions of 370,000 tons/year (340,000 tonnes) by up to 5 times.

4.5.1 Energy Savings

These energy savings and greenhouse gas emission reductions accrue from several sources. The most obvious source of energy savings is the improvement in pyrolysis furnace efficiency due to reduced fouling. Pyrolysis consumes 58% of the energy required for ethylene production and coking has been reported to produce a net decrease of 1% to 3% in furnace efficiency.^{3,9} Accordingly, it is reasonable to anticipate that the clad ODS tubes developed under the program

will produce an overall 1% increase in furnace efficiency—a factor of 2 reduction in the average 2% decrease in furnace efficiency due to coking. Taking the energy intensity of ethylene production in the United States to be 11,000 BTU/lb (26 GJ/metric ton), this represents an energy savings of 65 BTU/lb (150 MJ/metric ton) ethylene produced. In 2002, US production of ethylene was about 55 billion lbs (25 million tonnes).¹ As noted before, clad ODS tubes are expected to be initially most applicable to the small diameter, short-residence time tubes used in high-severity furnaces. Assuming such furnaces represent about 20% of domestic production capacity, total energy savings will be given by $(65 \text{ BTU/lb}) \times (5.5 \times 10^{10} \text{ lb}) \times 0.20 = 0.7 \text{ trillion BTU}$ [$(150 \times 10^6 \text{ J/tonne}) \times (25 \times 10^6 \text{ tonnes}) \times (0.20) = 7.5 \times 10^{14} \text{ J}$].

In addition, the bimetallic tubes will reduce the amount of hydrocarbon feedstock wasted by conversion into coke. Ren and coworkers estimate that 1 – 2% of total hydrocarbon feedstocks are lost by conversion into coke.²² Assuming the bimetallic tubes reduce the extent of coking by a factor of 2, this represents a decrease of $1.5\% / 2 = 0.8\%$ in the amount of required hydrocarbon feedstock for ethylene production. Further assuming an 82% conversion efficiency from hydrocarbon feedstocks, this represents a decrease of 1% in the amount of required feedstock. Taking domestic ethylene production in short-residence-time furnaces to be $0.2 \times 55 \text{ billion lbs}$ ($0.2 \times 25 \text{ million tonnes}$), this represents an increase of 110 million lbs (50,000 tonnes) in hydrocarbon feedstocks. If the majority of this feedstock has a fuel value (low heating value) of 21,000 BTU/lb (48 MJ/kg) similar to ethane, this represents an energy equivalent of 2.3 trillion BTU per year ($2.4 \times 10^{15} \text{ J/year}$), about three times the energy savings due to improved furnace efficiency.²³

Reducing the extent of coking also reduces the amount of energy required to heat feedstocks ultimately converted to coke, as well as to heat pyrolysis furnaces during decoking cycles. As noted above, the bimetallic tubes are anticipated to reduce the amount of hydrocarbon feedstocks required by about 0.8% for short-residence-time furnaces. The energy saved by not heating these feedstocks will be $(0.008) \times (0.58 \text{ fraction energy consumed in pyrolysis}) \times (1.1 \times 10^4 \text{ BTU/lb}) \times (55 \text{ billion lbs ethylene/yr}) \times (0.20) = 0.56 \text{ trillion BTU/yr}$ [$(0.008) \times (0.58 \text{ fraction energy consumed in pyrolysis}) \times (26 \times 10^9 \text{ J/tonne ethylene}) \times (25 \times 10^6 \text{ tonnes ethylene/yr}) \times (0.20) = 6 \times 10^{14} \text{ J per year}$]. This is just slightly less than the amount of energy saved through improved furnace efficiency. Actual energy savings are likely to be greater than this, since feedstocks (and steam) which do not need to be heated in the pyrolysis furnace also do not need to be processed by the downstream separation and purification equipment in the plant.

Reducing the amount of coke buildup in the pyrolysis furnace also reduces the amount of energy required to heat the furnace during decoking cycles. Ren estimates that 1% to 2% of total energy usage for ethylene production is utilized for decoking/defouling, shutdowns/restarts and related maintenance.²² This appears reasonable, since a 1-day decoking cycle every 65 days corresponds to 1.5% of the total furnace cycle time. If bimetallic tubes reduce the extent of coking by a factor of 2, this represents an average energy savings of $1.5\% / 2 = 0.8\%$ in total energy usage. As with the energy savings due to reduced heating of feedstocks, this represents an annual energy savings of 0.56 trillion BTU/year ($6 \times 10^{14} \text{ J/year}$). Note that this reduction in downtime also represents a significant increase in productivity for operators of ethylene plants, recovering an estimated \$44 million/yr in lost productivity for these short-residence time furnaces.

Summing these four components, total energy savings for the bimetallic pyrolysis tubing technology will be on the order of 4.1 trillion BTU (4.3×10^{15} J) per year. These energy savings also translate directly into reductions in greenhouse gas emissions. Even the 2.3 trillion BTU/year (2.4×10^{15} J/year) energy-equivalent savings of the feedstocks not converted to coke actually translates into a reduction in greenhouse gas emissions, since most deposited coke is ultimately combusted to CO₂ during decoking operations. Accordingly, the bimetallic tube technology also has potential for saving 370,000 tons (340,000 tonnes) of CO₂ emissions per year. Additional energy savings and CO₂ emission reductions may also accrue from improved heat transfer through thinner-walled tubes due to the higher strength of the tubing alloys and lower pressure drops across the furnace coils.

4.5.2 User Requirements for Bimetallic Tubes

At the start of this development program, it was envisioned that the inner core of the bimetallic tubes would be quite thin—on the order of 1 mm or less—and that the majority of the tube would consist of ODS Alloy 803. Commercialization work done under the program has shown that this initial concept is not correct. At least some user organizations will require a much thicker inner layer—probably on the order of at least 3 mm—to ensure that this inner layer remains intact for the life of the tube. This change has significant implications for tubing development. First, it suggests that the limited fabricability of the Incoloy[®] MA956 core may become an issue for some applications. As noted earlier, it also suggests that the extruded bimetallic tubes will need to be produced using a powder/powder rather than a tube/powder approach.

At the start of the program, it was also anticipated that the bimetallic ODS tubes being developed would be attractive to user organizations for BOTH their reduced coking AND increased temperature capability. Indeed, a major driving force for focusing development work on the Incoloy[®] MA956 / ODS Alloy 803 system rather than something like the more straightforward Incoloy[®] MA956 /Alloy 803 system was to exploit the higher temperature capability of the ODS alloys. It was expected that pyrolysis furnace users and manufacturers would judge the improved furnace productivity enabled by the higher temperatures to be of significant value.

At least in the short term, this has proven not to be the case. Since pyrolysis furnaces are generally designed for a specific operating temperature, higher-temperature tubing materials are primarily of interest for new furnace construction rather than for retubing applications. At present, few new ethylene pyrolysis furnaces are being constructed in the United States. Furthermore, those furnaces which are being built are likely to be designed primarily for ethane processing, where wrought small-diameter furnace tubes like those being developed under the program offer less of an advantage. Even the potential increased service life of ODS pyrolysis tubes has been found to be less attractive to potential customers than anticipated. Current centrifugally-cast pyrolysis furnace tubes generally exhibit a service life of 5 to 7 years. Ethylene producers appear reluctant to pay ANY sort of a cost premium for higher-performance tubes, since they have found that furnace technology also seems to improve significantly about every 5 to 7 years. Accordingly, current tubes need to be replaced at just about the same time as the furnace needs to be upgraded in order to remain competitive. In today's environment of rising fuel and feedstock prices, ethylene producers appear to have limited opportunity to invest in new, higher-temperature or longer-life alternatives to current centrifugally-cast radiant coils.

Instead, current furnace and ethylene producers appear focused primarily on exploring tubing materials which can reduce operating costs through reduced coking. If bimetallic ODS tubes like those explored under this program are to be marketed primarily on their reduced coking characteristics rather than on their improved temperature capability or extended service life, it may be advantageous for these materials to exhibit more than the factor of 2 decrease in coking rate targeted in the initial proposal and demonstrated under this program.

5.0 Accomplishments

This program successfully demonstrated that an oxide dispersion strengthened variant of Alloy 803 can be produced and processed to exhibit the coarse, elongated grain structure required for optimum high temperature creep resistance. The work also demonstrated that bimetallic oxide dispersion strengthened tubes can be produced by direct powder extrusion of a tubular can, and that Incoloy[®] MA956 does, in fact, exhibit reduced coking compared to conventional wrought Fe-Ni-Cr alloys. Findings of the program were disseminated to the technical community through publication of two papers, presentation of four technical talks and submission of one invention disclosure. The work will also result in one M.S. thesis. These are listed below:

Publications

- 2005 M. McKimpson, M. King and C. Arthur, "Processing and Characterization of Oxide Dispersion Strengthened Alloy 803" (in) L. Shaw et. al. (ed.), *Science and Technology of Powder Materials: Synthesis, Consolidation and Properties*, Warrendale, PA, 2005. pp. 79-86.
- 2003 M. McKimpson and M. King, "Instrumented Mechanical Alloying of a Novel Superalloy Powder", (in) F. Marquis (ed.), *Powder Materials: Current Research and Industrial Practices III*, TMS, Warrendale PA, 2003. p. 273-290.

Presentations

- 2005 "Processing and Characterization of Oxide Dispersion Strengthened Alloy 803", Materials Science and Technology 2005, Pittsburgh, PA, September 27, 2005.
- 2004 "Development of Co-Extruded, Oxide Dispersion Strengthened Tubes for Ethylene Pyrolysis", Materials Science & Technology 2004, New Orleans, LA, September 27, 2004.
- 2004 "Future Coils for Ethylene Furnaces: Reduced or No Coking and Increased Coil Longevity", Chemistry of Coke and Carbon Deposition in Fuel Systems and Process Units—228th American Chemical Society ACS Meeting, Philadelphia PA, August 24, 2004.
- 2003 "Instrumented Mechanical Alloying of a Novel Superalloy Powder", Materials Science & Technology 2003, Chicago, IL, November 12, 2003.

Patent

One invention disclosure was filed with Michigan Technological University covering the concept of using matched-density oxides as dispersoids in oxide dispersion strengthened materials such as ODS Alloy 803.

Thesis

Mr. Cory Arthur, a student at Michigan Technological University, is currently preparing an M.S. thesis entitled "Study of Clad Tubing Extrusion Using the Finite Element Method" based on the modeling work which he completed under the program. This thesis is expected to be completed by Summer 2006.

6.0 Conclusions

1. This work has demonstrated that an oxide dispersion strengthened variant of Alloy 803 can be produced successfully using conventional mechanical alloying technology. ODS Alloy 803 powders can be produced in an attritor using blended elemental charge materials and a commercially-available yttrium oxide dispersoid. These powders can then be consolidated successfully by direct powder extrusion using practices similar to those used for current commercial ODS alloys. The consolidated material can be recrystallized to a largely coarse-grained microstructure by annealing at 1300°C for about 1 hr.
2. An approach has also been demonstrated for producing bimetallic Incoloy[®] Alloy MA956 / ODS Alloy 803 tubes by direct powder co-extrusion. Both large-strain finite element simulation and experimental trials showed that bimetallic tubes can be produced using a powder/powder approach in which concentric rings of Incoloy[®] MA956 powder and ODS Alloy 803 powder contained in a tubular can are direct-extruded using a mandrel. Extrusion of bimetallic tubes using a powder/tube approach with an inner solid tube of Incoloy[®] MA956 was surrounded by an outer ring of ODS Alloy 803 powder was less successful. The work also showed that the DEFORM finite element software package could be used fairly successfully to simulate isothermal extrusion of porous bimetallic tubular billets and non-isothermal extrusion of solid bimetallic billets. Additional work is needed, however, to more fully develop this novel extrusion technology.
3. Coking trials conducted under the program confirmed that pre-oxidized Incoloy[®] MA956 exhibits a rate of coke buildup at least 50% lower than that observed on chromia-forming alloys such as Incoloy[®] 800. A computer-controlled, thermogravimetric-based coking test rig was constructed under the program and used to assess the coking rate of the Incoloy[®] MA956 alloy compared to Incoloy[®] 800 in an equimolar N-butane/steam mixture at 800°C. Mass change measurements showed the rate of coke buildup on the Incoloy[®] MA956 to be about 1/3 that observed on the Incoloy[®] 800 over a 7-hour test period. The TGA data also showed that the rate of coke buildup on both the Incoloy[®] MA956 and Incoloy[®] 800 was constant over the test interval.
4. Gas tungsten arc welding trials performed on ODS Alloy 803 extruded bars and bimetallic Incoloy[®] MA956 / ODS Alloy 803 co-extruded tubes showed that alternate joining strategies need to be explored for these materials. At the start of the program, it was expected that the ODS Alloy 803 material would exhibit welding characteristics similar to those of wrought Alloy 803. This was found not to be the case. Rather, both the ODS Alloy 803 and bimetallic tube showed dispersoid agglomeration and porosity in the fusion zone of the weld. Accordingly, work was undertaken to explore the use of matched-density oxide dispersoids in the ODS Alloy 803, and an invention disclosure was filed with Michigan Technological University covering this approach. Additional work is needed, however, to develop this approach.
5. The program provided a much more complete understanding of the requirements for successful commercialization of high-performance radiant tubes for ethylene pyrolysis service. Bimetallic tubes containing an inner core of coking-resistant Incoloy[®] MA956 are likely to require an Incoloy[®] MA956 layer at least 3 mm thick to insure that this layer remains intact throughout the lifetime of the tube. In today's competitive environment,

pyrolysis furnace manufactures and ethylene producers appear somewhat reluctant to pay any sort of cost premium for higher-performance coil materials offering higher temperature capabilities or longer service life.

7.0 Recommendations

The oxide dispersion strengthened bimetallic radiant coil concept explored under this program continues to have significant long-term potential for energy savings and productivity improvements for domestic ethylene producers. In today's competitive market, however, domestic furnace manufacturers and ethylene producers appear to be placing primary emphasis on shorter-term, lower-risk technology fixes offering reduced operating expenses with little or no increase in acquisition cost.

Interest in oxide dispersion strengthened radiant coils like those investigated under this program will increase significantly when furnace and ethylene producers begin focusing on increasing tube wall temperatures as a means of improving furnace productivity. This is likely to be driven by increased interest in very-short-residence-time furnaces such as those used to process naphtha-based feedstocks.

Continued development of oxide dispersion strengthened radiant coils should focus in several areas. First, coking studies should be continued to develop an improved understanding of both the coking behavior and the potential for anti-coking pretreatments on ODS alloys such as Incoloy[®] MA956 and ODS Alloy 803. Extrusion work on bimetallic tubes and joining studies on the ODS materials also need to be continued. For joining, the matched-density dispersoid concept appears to have some potential, as does the use of novelly-configured tapered joints. To expand commercial markets and lower the cost of oxide dispersion strengthened alloys such as ODS Alloy 803, work should also be undertaken to explore other commercial markets for these materials, including heat treatment fixtures and elevated temperature metalworking tooling.

Future work in any of these areas should be undertaken using a consortium approach involving a broad range of stakeholders, including ethylene producers, furnace manufacturers, material producers and research organizations. Organizing future work through a group such as the Materials Technology Institute of the Chemical Process Industries, Inc., would be extremely beneficial.

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