NEW MATERIALS AND PROCESSES

PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT TITLE: Advanced Industrial Materials (AIM) Fellowship Program

PHASE: FY 1998 **COMPLETION DATE:**

PERFORMING ORGANIZATIONS: Oak Ridge Institute for Science and Education, Oak Ridge, Tennessee; Virginia Polytechnic Institute and State University, Blacksburg, Virginia; University of Cincinnati, Cincinnati, Ohio; University of Alabama, Tuscaloosa, Alabama; Oak Ridge National Laboratory, Oak Ridge, Tennessee.

PRINCIPAL INVESTIGATORS: D. D. McCleary, Oak Ridge Institute for Science and Education; M. K. Lian, Virginia Polytechnic Institute and State University; A. Jordan and O. N. C. Uwakweh, University of Cincinnati; and P. J. Maziasz and D. F. Wilson, Oak Ridge National Laboratory.

PHASE OBJECTIVE: The Graduate Fellowship Program focused toward helping students who currently are under-represented in the nation's pool of scientists and engineers, enter and complete advanced degree programs.

ULTIMATE OBJECTIVES: The objectives of the program are to: (1) establish and maintain cooperative linkages between DOE and professors at universities with graduate programs leading toward degrees or with degree options in Materials Science, Materials Engineering, Metallurgical Engineering, and Ceramic Engineering, the disciplines most closely related to AIM Program objectives at Oak Ridge National Laboratory (ORNL); (2) strengthen the capabilities and increase the level of participation of currently underrepresented groups in master’s degree programs; and (3) offer graduate students an opportunity for practical research experience related to their thesis topics through the 3-month research assignment or practicum at ORNL. The Oak Ridge Institute for Science and Education (ORISE) administers the program.

TECHNICAL APPROACH: Offer fellowships for master’s degree program in materials science–related academic fields.

PROGRESS: Three fellowship recipients are involved in the project.

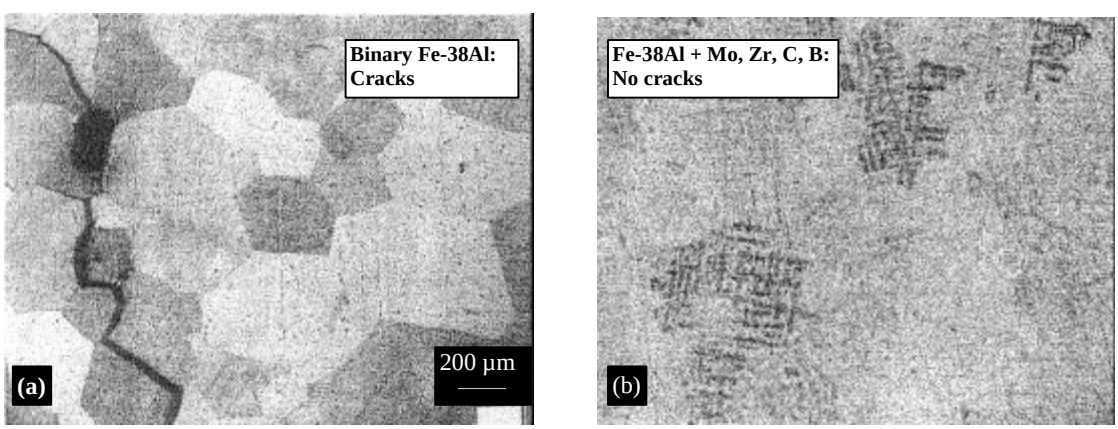
SIGNIFICANT ACCOMPLISHMENT

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

AIM Fellowship Program: Cast FeAl Alloys Show Improved Weldability

ISSUE: FeAl iron-aluminides have outstanding oxidation, sulfidation, and carburization resistance at 1000°C and above due to protective Al_2O_3 scale formation. But, can FeAl alloys be welded? Do the alloy additions that improve ductility and toughness at room-temperature enable them to survive cold cracking after welding?

RESULTS: New cast FeAl alloys (Fe– 36 to 40 at. % Al) designed for improved high-temperature strength and room-temperature ductility were developed that showed good tensile strength at 700 to 1000°C, and creep strength at 700 to 800°C. Such complex cast FeAl alloys (with additions of Mo, Zr, C, and B) were found to have up to 4 to 5% ductility in air at room temperature, and about 10 to 15 J Charpy impact toughness, or more. While such cast FeAl alloys have been found to be weldable without any cold cracking after appropriate heat treatment, their behavior is not well understood. As part of this ORISE Ph.D. Minority Fellowship Program work, Gleeble simulations of the weld-cylce were conducted on the complex, cast FeAl alloys, and a series of simpler alloys with each of the critical solutes removed to reach the equivalent binary FeAl alloy. As shown below, the binary FeAl alloy developed severe cold cracking, with brittle fracture occuring along grain boundaries. By contrast, the complex alloy with B, C, Mo, and Zr shows no such cracking. Intermediate alloys with only Mo added do crack, but then all the alloys with B and/or C do not crack. This study clearly confirms and shows that B and C together are critical elements for preventing grain-boundary fracture and increasing ductility at room temperature, both of which are needed for resistance to cold cracking during welding.



Gleeble Weld Simulation

Research performed at the University of Cincinnati, sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials Program, under contract DE-AC05-96OR22464 with Lockheed-Martin Energy Research Corporation.

PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT TITLE: Advanced Materials for High-Temperature Liquid-Metal Corrosion and Erosion Resistance

PHASE: FY 1998 **COMPLETION DATE:**

PERFORMING ORGANIZATION: Los Alamos National Laboratory

PRINCIPLE INVESTIGATORS: M. Trkula (505-667-0591) and M. Nastasi (505-667-7007)

PHASE OBJECTIVE: To develop novel plasma-based surface engineering technologies for the production of corrosion- and erosion-resistant, thermodynamically stable, and highly adherent conformal coatings on die materials used to cast aluminum and other metals.

ULTIMATE OBJECTIVE: To produce a cost-effective and industrially relevant surface-engineering process through the combination of materials science, plasma-immersion processing, and organometallic chemical vapor deposition (OMCVD) techniques. This process should be non-line-of-sight to allow easy processing of complex shapes and should also be inherently scaleable to allow for the processing of extremely large components. The immediate objective is to develop corrosion- and erosion-resistant, thermodynamically stable, and highly adherent conformal coatings on die materials used to cast aluminum and other metals. Follow-on objectives may include development of wear, erosion, and reduced-friction coatings.

TECHNICAL APPROACH: Candidate corrosion- and erosion-resistant coatings will be chosen based on an analysis of thermodynamic and thermal expansion for the total system of liquid metal/coating/substrate. Coating synthesis will employ a combination approach using OMCVD with plasma-immersion ion processing (PIIP). The PIIP process will be used to physically and chemically clean the substrate surface, ion-implant coating species into the substrate surface to provide a graded transition to the coating, and deposit thick, adherent, and conformal surface coatings when used in conjunction with OMCVD.

PROGRESS: Discussions between Los Alamos and a variety of industries have been on-going over the last year. These industries include Ford Motor Company, Chrysler, Empire Hard Chrome, Alcoa, Reynolds, Boeing Corporation, and Schlumberger. A *Commerice Business Daily* advertisement was published on this project, and we are reviewing the responses. A CRADA between LANL and Pratt and Whitney is in progress.

Patents: None. **Publications:** None **Proceedings:** None.

Books: None. **Presentations:** 3 **Awards:** None.

PROJECT SUMMARY (continued)

PROJECT TITLE: Advanced Materials for High-Temperature Liquid-Metal Corrosion and Erosion Resistance

ACCOMPLISHMENTS: Coatings of AlN, Er_2O_3, B-C-H, and Cr-C-O have been produce on a variety of substrate materials. Wetting experiments show that Cr-C-O coatings provide effective protection against reactions between molten Al and steel substrates. B-C-H coatings were found to be not effective. The AlN deposition conditions were varied to minimize hydrogen content. The Er_2O_3 was found to be stoichiometric.

Licenses: None. **Known Follow-On-Product(s):** None.

Industry Workshops: None. **Technology Transfer or Industrial Interactions:** None.

CRITICAL ISSUES: Production of Cr-C-O coatings that inhibit wetting and soldering of molten Al when in contact with steel-based substrates.

FUTURE PLANS: To investigate further the synthesis of Cr-C-O coatings and evaluate their properties. We plan to determine the role of deposition parameters on the coating composition, deposition rate, ultimate coating thickness, surface mechanical properties (i.e., hardness, wear resistance, and friction), coating adhesion, and delamination, and Al wetting properties.

POTENTIAL PAYOFF: The potential payoff for industrial application in the area of Al die casting is anticipated to be very high. The development of a low-cost surface-engineering process for the production of non-wetting and erosion-resistant surface coatings is highly desirable. Cost savings can be realized from the extension of die life, reduced energy losses due to thermal cycling, and the improved surface finish of the cast product.

ESTIMATED ENERGY SAVINGS: We have studied material lifetime and its effect on aluminum die casting in the automotive industry. Estimates indicate that dye life extension for this industry alone can result in energy savings of 3.3×10^{12} to 3.3×10^{13} Btu/year.

SIGNIFICANT ACCOMPLISHMENT

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

Plasma Processing—Advanced Materials for Corrosion and Erosion Resistance

ISSUE: Die life is a major consideration in the die casting process. Die degradation occurs principally by thermal fatigue (i.e., heat checking), erosive and abrasive wear, chemical attack and/or corrosion, and soldering between the die and casting material. Our approach to solving this problem is to develop novel plasma-based surface-engineering technologies for the production of corrosion- and erosion-resistant, thermodynamically stable, and highly adherent conformal coatings on die materials used to cast aluminum and other metals.

RESULTS: Synthesis of a Cr-C-O coating was accomplished through the combined approach of using organometallic chemical vapor deposition (OMCVD) with plasma-immersion ion processing (PIIP). The organometallic chemical source for this coating was $Cr(CO)_6$. The PIIP process was used to sputter clean the substrate surface prior to coating deposition, to provide plasma generation of the $Cr(CO)_6$ gas and to supply a substrate bias voltage during coating deposition. The figure shows the results of wetting experiments between molten Al and steel substrates, both with and without the PIIP-generated Cr-C-O coating. The data show that Cr-C-O coating provides effective protection against reactions between molten Al and 304 stainless steel substrates.

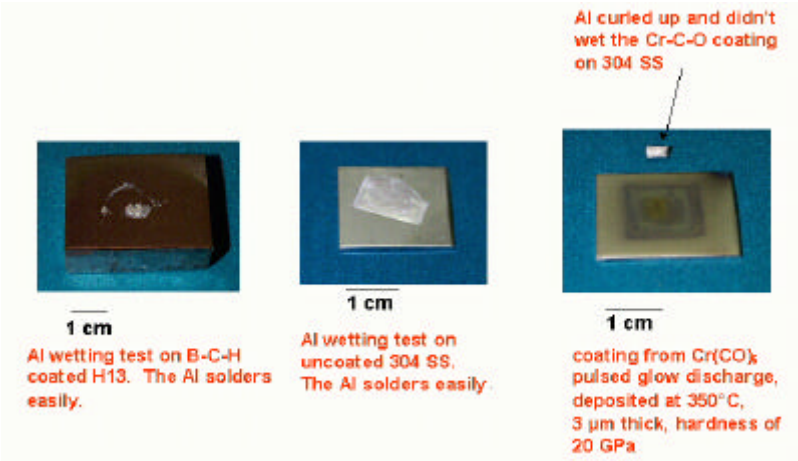


Fig. 1. Molten aluminum wetting test for B-C-H– and Cr-Co–coated steel substrates and an uncoated 304 stainless steel substrate.

ESTIMATED ENERGY SAVINGS: We have studied material lifetime and its effect on aluminum die casting in the automotive industry. Estimates indicate that die life extension for this industry alone can result in energy savings of 3.3×10^{12} to 3.3×10^{13} Btu/year.

Research performed at Los Alamos National Laboratory, sponsored by the U.S. Department of Energy under programs from the Office of Energy Efficiency and Renewable Energy/Office of Industrial Technologies and Office of Basic Energy Science/Division of Materials Science.

PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT TITLE: Development of Improved Refractories

PHASE: FY 1998 **COMPLETION DATE:**

PERFORMING ORGANIZATIONS: Oak Ridge National Laboratory (ORNL) and the University of Missouri at Rolla (UMR).

PRINCIPAL INVESTIGATOR(S): Andrew A. Wereszczak/ORNL (423-574-7601 and Robert E. Moore/UMR (573-341-4401).

PHASE OBJECTIVE: Conduct compressive creep, corrosion, and dimensional stability studies on conventional silica refractories (a "category"). Perform pre- and post-testing analyses to correlate microstructural changes with the determined creep, corrosion, and dimensional stability performances.

ULTIMATE OBJECTIVE: Generate an engineering database on the thermomechanical and thermophysical properties of several different commercial refractory categories that are candidate materials for glass-melting furnace superstructures.

TECHNICAL APPROACH: High-temperature mechanical engineering data will be generated on competing brands of commercially available refractories that are candidate materials for glass-furnace superstructures. The creep rate of these materials will be measured as a function of stress and temperature; chosen stresses and temperatures will bracket those that exist during service in the superstructure. The data will be made available to glass manufacturers so that they may (1) make equitable comparisons of competing brands that would facilitate their choice of refractory brand for their applications and (2) provide design data to their furnace-design-engineers to use for optimizing superstructure design.

PROGRESS: In the first study of its kind, an objectively generated systematic creep and dimensional study of conventional silica refractories was completed. Historically, conventional silica has been the primary refractory used for furnace superstructures; however, engineering creep studies describing their performances are essentially nonexistent in the literature. The employed test temperatures and stresses comprising the test matrix bracketed those of furnace superstructure service. It was determined that the amount of compressive creep of the examined brands was quite small (for Type A conventional silicas) and equivalent among them at 1550 to 1650°C and 0.2 to 0.6 MPa. All brands exhibited a time-dependent, permanent net expansion due to exposure to temperature. The amount of this expansion was much greater than the permanent contraction that they exhibited during compression creep. These results indicate that conventionally used creep-deformation models are inappropriate for predicting the total long-term deformation of these silica refractories because creep is such a small fraction of their overall dimensional stability. Lastly, the corrosion resistances among these brands were equivalent up to 1400°C.

PROJECT SUMMARY (continued)

PROJECT TITLE: Development of Improved Refractories

Patents: None.	**Publications:** 1	**Proceedings:** None.
Books: None.	**Presentations:** 2	**Awards:** None.

ACCOMPLISHMENTS: The primary accomplishment in FY 1998 was the completion of compression creep testing of competing conventional silica brands. The data currently are undergoing analyses, and the findings will be supplied to glass-manufacturing engineers involved in the design of furnace superstructures. The data will help them choose optimum refractory materials for the promotion of longer-term service of their furnaces.

Licenses: None. **Known Follow-on Product(s):** None. **Industry Workshop:** None.

Technology Transfer or Industrial Interaction: None.

CRITICAL ISSUES: For future testing of fusion-cast alumina refractories, the critical issue will be the determination and understanding of microstructural variation as a function of position within the cast alumina blocks. This will result in the creation of another independent parameter (along with temperature and stress) in the examination of refractory creep performance.

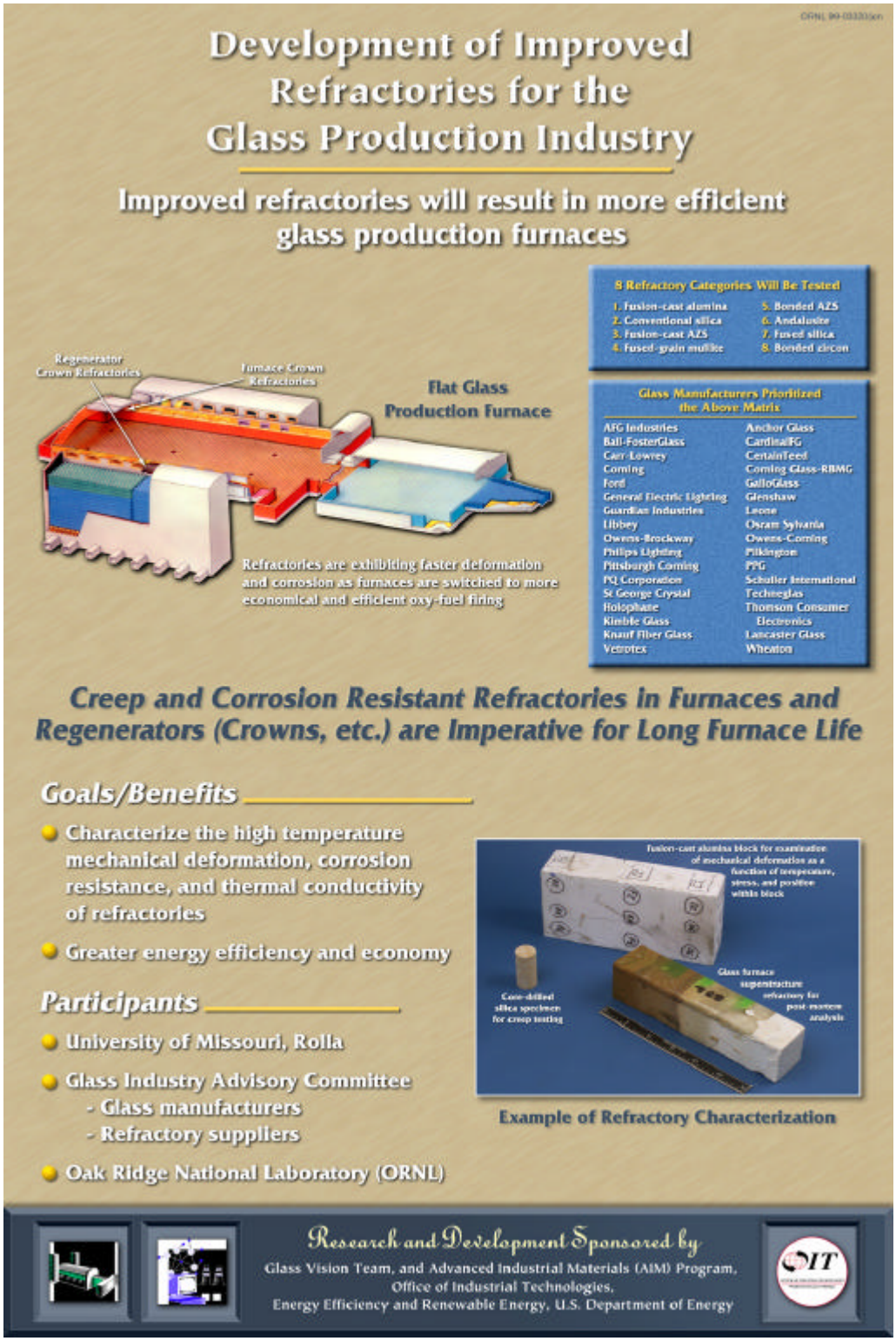
FUTURE PLANS: With the refractory categories identified (eight in all; one now completed), fusion-cast alumina and mullite refractories will be tested next. Additionally, specimens will be subjected to service environments, and their corrosion resistance will be examined. Dimensional stability in the absence of stress of these refractories also will be characterized.

POTENTIAL PAYOFF: More efficient and economical designs of glass-melting furnace superstructures will be a consequence of this project. Furnace superstructure designers will know which refractory brands perform better than others (from objectively generated data). Additionally, accurate engineering data will be available to describe the high-temperature mechanical performance of candidate refractory materials and furnace superstructures made from them.

ESTIMATED ENERGY SAVINGS: Based on the 1998 DOE/OIT GPRA Report, approximately $202M in energy savings per year in 2005 and a $445M per year savings by 2020 will be realized with the conversion of air/fuel– to oxy-fuel–fired furnaces. These results come from the consideration that 61% and 100% furnace conversions will occur by the years 2005 and 2020, respectively. Glass manufacturers and their furnace designers will use the results from this project to accelerate this conversion process.

SIGNIFICANT ACCOMPLISHMENT

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM



PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT TITLE: Materials R&D¾ Student Internships

PHASE: FY 1998 **COMPLETION DATE**: September 30, 1998

PERFORMING ORGANIZATION: Ames Laboratory

PRINCIPAL INVESTIGATORS: R. Bruce Thompson (515-294-9649), I. E. Anderson (515-294-4446), and T. E. Bloomer

PHASE OBJECTIVE: To continue programmatic research while educating students.

ULTIMATE OBJECTIVE: To conduct programmatic research of significance to the Advanced Industrial Materials Program while training under-represented graduate students in the process.

TECHNICAL APPROACH: The approach for involving students is recruiting for participation in the program, matching them with projects of programmatic interest to the AIM Program, conducting the research, continuous mentoring, and graduation. The specific technical approach will depend on the projects selected. The primary work in the current year is directed towards improving the mechanical properties of SnAgCu + Co, a new lead-free solder.

PROGRESS: Initial studies of the microstructure and mechanical properties of SnAgCu + Co, a new lead-free solder, have been conducted. When compared to the Sn-Pb eutectic and other Pb-free solders, a new alloy SnAgCu has been found to have improved strength and very good resistance to microstructural coarsening at high temperature (125°C). Minor additions of the transition metal Co allows mechanical and microstructural stability to be maintained to 170°C with double the ultimate tensile strength of the SnPb eutectic, and preliminary evidence suggests improved fatigue properties.

Publications: 1

ACCOMPLISHMENTS:

Licenses: None. **Known Follow-On Products:** Solder in wire, paste, ingot.

Industry Workshop: None.

Technology Transfer or Industrial Interaction: Discussions with Multicore Solders, Hector Steen; Johnson Manufacturing, Al Gickler; and Nihon Superior, Tetsuro Mishimura.

PROJECT SUMMARY (continued)

PROJECT TITLE: Materials R&D¾ Student Internships

CRITICAL ISSUES: Identifying appropriate students and assisting them in what can be a significant transition from their undergraduate institution to a major research university.

FUTURE PLANS: Continued recruitment and education of under-represented students.

POTENTIAL PAYOFF: Increasing the fraction of the population available to perform technical jobs for the nation.

SIGNIFICANT ACCOMPLISHMENT

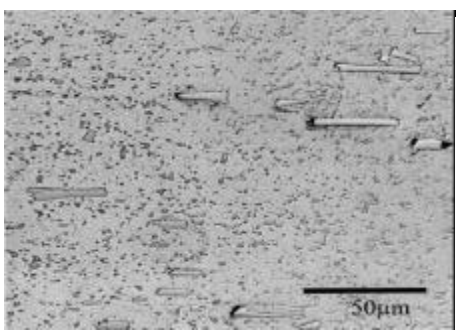
ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

Materials R&D—Student Internship

ISSUE: Microstructural and Mechanical Properties of Tin-Silver-Copper + Transition Metal Solder

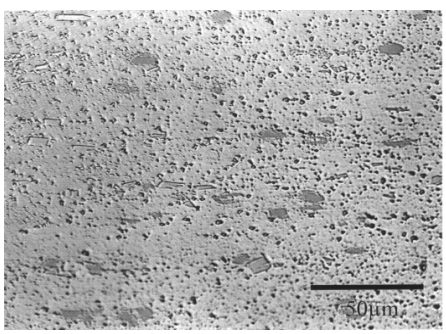
RESULTS: The overall results to date indicate that SnAgCu+Co solder alloys have superior performance over all other alloys tested. They show increased hardness, without significant loss in ductility. Good mechanical and microstructural stability is maintained to 170ºC. As-drawn wire samples of the Sn–4.7Ag–1.7Cu (wt %) eutectic composition with and without small Co additions (<0.5 wt %) show fine homogeneously distributed spheres of Ag_3Sn and blocky Cu_6Sn_5 in a matrix of tin. The Cu_6Sn_5-phase particles align in the drawing direction. Co additions refine this as-drawn microstructure, and, during annealing of the wire samples, the Ag_3Sn spheres coarsen while the Cu_6Sn_5 do not grow appreciably in size. Addition of Co creates an apparent partitioning effect in the Cu_6Sn_5 phase, creating a core of Co-rich $(Cu+Co)_6Sn_5$ with almost pure Cu_6Sn_5 around the edges.

The room-temperature tensile tests of as-drawn wire samples clearly show that even minor additions of Co to SnAgCu can double the ultimate tensile strength over that of SnPb eutectic. Also, SnAgCu + Co solder wire ductility is within the same range as SnPb, predicting a significant improvement in fatigue strength that must be verified by further testing.

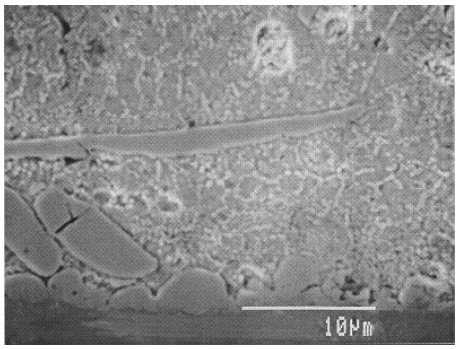


(a) Sn–4.7Ag–1.7Cu

Fig. 1. Optical photos of as-drawn wire longitudinal cut: (a) Sn–4.7Ag–1.7Cu and (b) Sn–4.7Ag–1.7Cu + 0.3Co. Note the microstructural refining effect created by the Co addition.

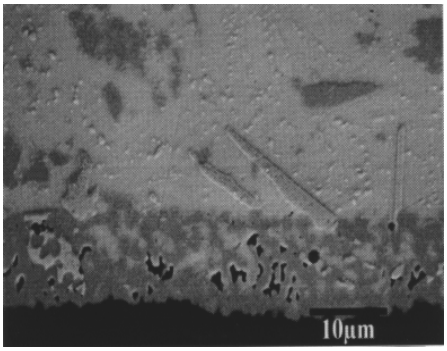


(b) Sn–4.7Ag–1/7Ci + 0.3Co



(a) SnAgCu

Fig. 2. SEM image of (a) SnAgCu and (b) SnAgCu + Co as-solidified solder joint interface. Note change in interface morphology with addition of Co.



(b) SnAgCu + Co

PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT TITLE: Metals Processing Laboratory User (MPLUS) Facility

PHASE: FY 1998 **COMPLETION DATE:**

PERFORMING ORGANIZATION: Oak Ridge National Laboratory (ORNL)

PRINCIPAL INVESTIGATOR: G. Mackiewicz-Ludtka (423-576-4652) and H. W. Hayden (423-574-6936)

PHASE OBJECTIVE: Continue to partner with DOE Vision Industries and Universities by providing access to the unique Technical Expertise and Facilities at MPLUS.

ULTIMATE OBJECTIVE: To assist U.S. industries in improving energy efficiency and enhancing their competitiveness in the global market by partnering with National Laboratories.

TECHNICAL APPROACH: Started as a small-scale, pilot User Facility Program in February 1996, MPLUS's initial goal was to determine whether a need existed for such a program, and, if so, to demonstrate its value. As of September 30, 1998, a total of 107 MPLUS Proposals were received from 60 different companies and universities representing states across the United States. The demand for and success of the MPLUS User Facilities continue and are evidenced by (a) the sheer number of users (61 companies); (b) the significant numbers (19 different) of organizations that requested repeated assistance and submitted multiple (2 to 5) proposals for different MPLUS projects; (c) the 4 companies that chose to do Proprietary (P) MPLUS projects, with 2 of these 4 P Users pursuing multiple P MPLUS projects.

PROGRESS: Due to continued industrial requests/needs and support, MPLUS has succeeded in demonstrating (within its 32 months of existence) that the unique technical expertise and facilities accessible through the National Laboratories are a valuable resource to U.S. industries. In fact, it is becoming quite clear, with the growing response and needs being identified via MPLUS, that MPLUS is a viable vehicle/mechanism to unite other National Laboratory User Facilities to provide industry with a mechanism to access these national resources as a *Distributed Laboratory*.

Patents: ERID0344	**Publications:** 13	**Proceedings:** 1
Books: None.	**Presentations:** ~12	**Awards:** 1

PROJECT SUMMARY (continued)

PROJECT TITLE: Metals Processing Laboratory User (MPLUS) Facility

ACCOMPLISHMENTS:

Licenses: None.

Known Follow-On Products: Some companies have funded several proprietary MPLUS projects at the conclusion of their nonproprietary project. Others have continued and/or built on the industrial/ORNL interactions and partnerships initiated through the MPLUS User Program, and they have been the catalysts for initiating additional partnering and collaborations among the industry, academia, and ORNL.

Technology Transfer or Industrial Interaction: Technology transfer and industrial interactions are what MPLUS is all about. They occur with every project.

CRITICAL ISSUES: Can National Laboratories be a valuable asset to U.S. industries by providing unique and valuable input to materials processing issues so that U.S. industries can reclaim their competitive edge in the global market?

FUTURE PLANS: Continue to expand MPLUS to incorporate additional needed facilities and expertise available at other sites.

POTENTIAL PAYOFF: Restoration of U.S. industry's competitive edge in the global market by providing a platform for enhanced relationships and partnerships among industries, academia, and National Laboratories. MPLUS also provides a mechanism for transferring R&D technologies into industrial arenas.

ESTIMATED ENERGY SAVINGS: Energy savings vary with the individual project. Some, like infrared-related projects, can and do realize immediate savings, not just in energy savings, but also in reducing negative impacts on the environment by replacing, reducing, and at times eliminating unit processes.

SIGNIFICANT ACCOMPLISHMENT

Advanced Industrial Materials (AIM) Program

PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT TITLE: Microwave Joining of SiC

PHASE: FY 1998 **COMPLETION DATE:**

PERFORMING ORGANIZATION: FM Technologies, Inc.

PRINCIPAL INVESTIGATOR: Richard Silberglitt (703-425-5111)

PHASE OBJECTIVE: To understand the nature of the SiC interlayer formed in situ from polymer precursor pyrolysis during microwave joining of SiC materials.

ULTIMATE OBJECTIVE: To identify and develop the most effective microwave-joining methods for scaling up to large tube assemblies of silicon carbide that are required for industrial applications.

TECHNICAL APPROACH: SiC was formed in situ by decomposition of polymer precursors in a microwave applicator evacuated and back-filled with inert gas. The quality of the SiC formed from different polymers was investigated via X-ray diffraction, and the shrinkage of the polymer was determined for input to stress analysis of three-dimensional joints (e.g., butt-plus-lap joint with collar) between SiC tubes.

PROGRESS: SiC was produced from several different polymer precursors, including three polycarbosilanes, two polysiloxanes, one polysilazane, and a polycarbosilane loaded with SiC particulates. The crystal development of the SiC was comparable to that produced using conventional heating, with the microwave-heated material showing a higher sensitivity to polymer carbon content. The 8-in. long, 1-in. OD, sintered SiC tubes joined under the HiPHES project were pulled to failure under tension at the High Temperature Materials Laboratory at Oak Ridge National Laboratory. One tube was tested at ambient temperature and the other seven at 1050°C. All failures were in the tubes or collars; no failures in the butt-plus-lap joint. Maximum loads at ambient and 1050°C were similar.

Patents: None. **Publications:** None. **Proceedings:** 1

Books: None. **Presentations:** 4 **Awards:** None.

ACCOMPLISHMENTS:

Licenses: None. **Known Follow-On Product(s):** None. **Industry Workshop:** None.

PROJECT SUMMARY (continued)

PROJECT TITLE: Microwave Joining of SiC

Technology Transfer or Industrial Interaction: Industrial-sponsored program is under development with Stone & Webster to join pairs of 15-ft–long, sintered SiC tube sections to form furnace coils for testing in a prototype high-temperature furnace in an ethylene production plant. Discussions are under way with INEX for application to reaction-bonded SiC radiant burner tube assemblies. Presentations were made at BES/CFCC Workshop, and discussions were held with CFCC contractors and program managers.

CRITICAL ISSUES: Development of applicators for cost-effective fabrication of industrial-size specimens and a full suite of mechanical strength data including service environment.

FUTURE PLANS: Joining of test specimens supplied by industrial collaborators that properly simulate the components to be fabricated, followed by tests conducted by the industrial collaborators that simulate performance environments, then scale up to fabricate prototype components, and finally prototype testing. Commercialization agreements will be based upon licensing or contract manufacturing, as appropriate.

POTENTIAL PAYOFF: The markets for SiC radiant burner tubes and heat exchangers have been estimated to be greater than $100 million annually. These components currently cannot be cost-effectively fabricated in lengths and shapes required. Microwave joining could be an enabling technology by allowing fabrication through the joining of several small, simply-shaped pieces. Development of a transportable microwave applicator would provide the capability for on-site fabrication and repair of ceramic tube assemblies.

ESTIMATED ENERGY SAVINGS: The DOE CFCC Program has estimated energy savings of 2 quads and energy cost savings of $8 billion for CFCC utility and industrial components. Natural gas savings are estimated at $173,000 per year due to the 4 to 7% higher efficiency of SiC radiant burner tubes. Use of a SiC tube heat exchanger in externally fired combined-cycle coal power plants is projected to produce a 20% increase in thermal efficiency. Energy savings through the reduction of feedstock consumption and decoke fuel and steam requirements with an advanced ethylene production process using a high-pressure SiC heat exchanger are projected to be 63.9 trillion Btu per year.

OTHER SOURCES: The State of Virginia Center for Innovative Technology and George Mason University have provided $165K in matching funds during this time period.

SIGNIFICANT ACCOMPLISHMENT

Advanced Industrial Materials (AIM) Program

ORNL 99-03386A/jcn

Microwave Joining of SiC Ceramics

Joined SiC Tubes Demonstrate High Temperature Strength

Applications:

- Radiant Burner Tubes
- Chemical Retort Tubes
- High Pressure Heat Exchangers
- Turbine Engine Components

Microwave Joining Apparatus

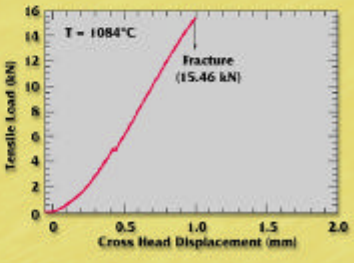
Benefits:

- Increased Energy Efficiency
- Increased Production Yield
- Decreased Downtime
- Natural Gas Savings

Joined SiC Tubes-3D Joints Connecting Sintered SiC Tubes Tested in Tension at 1050°C

CT Scan-Load to Failure at 1050°C Same as at Ambient Temperature

- Joined reaction bonded SiC tubes have fracture toughness equal to original material
- Sintered and composite SiC joined by making SiC during joining from pyrolysis of polymer material



Load-vs-Displacement in Tension-Lap Joints Survived Test (All Fractures Occurred at Collar or Tube)

Participants:

- FM Technologies
- Stone & Webster
- INEX, Inc.
- Oak Ridge National Laboratory (ORNL)
- Argonne National Laboratory (ANL)

Research and Development Sponsored by
Advanced Industrial Materials (AIM) Program,
Office of Industrial Technologies, U.S. Department of Energy

PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT TITLE: Selective Inorganic Thin Films

PHASE: FY 1998 (Materials Development) **COMPLETION DATE**: Open

PERFORMING ORGANIZATIONS: Sandia National Laboratories (SNL), Amoco Chemical Corporation (ACC), University of New Mexico (UNM), and University of Western Australia (UWA)

PRINCIPAL INVESTIGATOR: Tina M. Nenoff/SNL (505-844-0340)

PHASE OBJECTIVES: Model, synthesize, and characterize novel inorganic composite Zeolite/sol-gel thin-film membranes for hydrocarbon separations via molecular sieving. Confine permeability of film to zeolite crystals by increasing density of coverage and reducing gas permeability of matrix. Enhance permeability by decreasing film thickness while maintaining continuous coverage. Succeed in guaranteeing funding for the CRADA portion of this project through the DOE/Vision 2020: The Chemical Industry.

ULTIMATE OBJECTIVE: Develop new class of inorganic membranes for hydrocarbon and light-gas separations, and possibly catalysis. Use this technology to improve upon separation efficiencies and thermal stability currently available with polymer or oxide membranes, emphasizing application to petroleum and natural-gas refining. Transfer technology base to industry.

TECHNICAL APPROACH: Use computational modeling to select appropriate microporous phases for desired separation. Nucleate and crystallize zeolite and microporous phosphate–based phases via hydrothermal synthesis methods, using porous filters and gas membranes as supports for these films. Investigate novel microporous zinc phosphates as molecular sieves.

PROGRESS: During FY 1998 we have successfully synthesized defect-free zeolite/sol-gel composite thin-film membranes on a number of different substrates. Furthermore, we have synthesized highly oriented zeolite crystals upon supports. The films are thermally stable up to 500°C. The choice of zeolite for various target hydrocarbon separations were determined by molecular modeling of pore sizes and shapes. We also have built a permeation testing unit that can accommodate both tubular- and disk-shaped membrane supports, and we can test both light-gas molecules and hydrocarbons from room temperature to 200°C.

Also during FY 1998, the team was awarded a 3-year, $4.295M grant from DOE/Vision 2020: The Chemical Industry to fund an existing CRADA. The CRADA was expanded to include Sandia, Amoco, and Coors Technical Ceramics Company, with industry contributing 56% in-kind funding.

PROJECT SUMMARY (continued)

PROJECT TITLE: Selective Inorganic Thin Films

ACCOMPLISHMENTS:

Publications: 1 **Presentations:** 4 **Disclosures:** 2 **Licenses:** None.

Known Follow-On Products: None. **Industry Workshops:** None.

CRITICAL ISSUES: (1**)** Development of defect-free inorganic composite zeolite/sol-gel membranes for specific hydrocarbon separations. (2) Award of funding from Vision 2020: The Chemical Industry for the CRADA membrane project (including Sandia, Amoco, and Coors Ceramics).

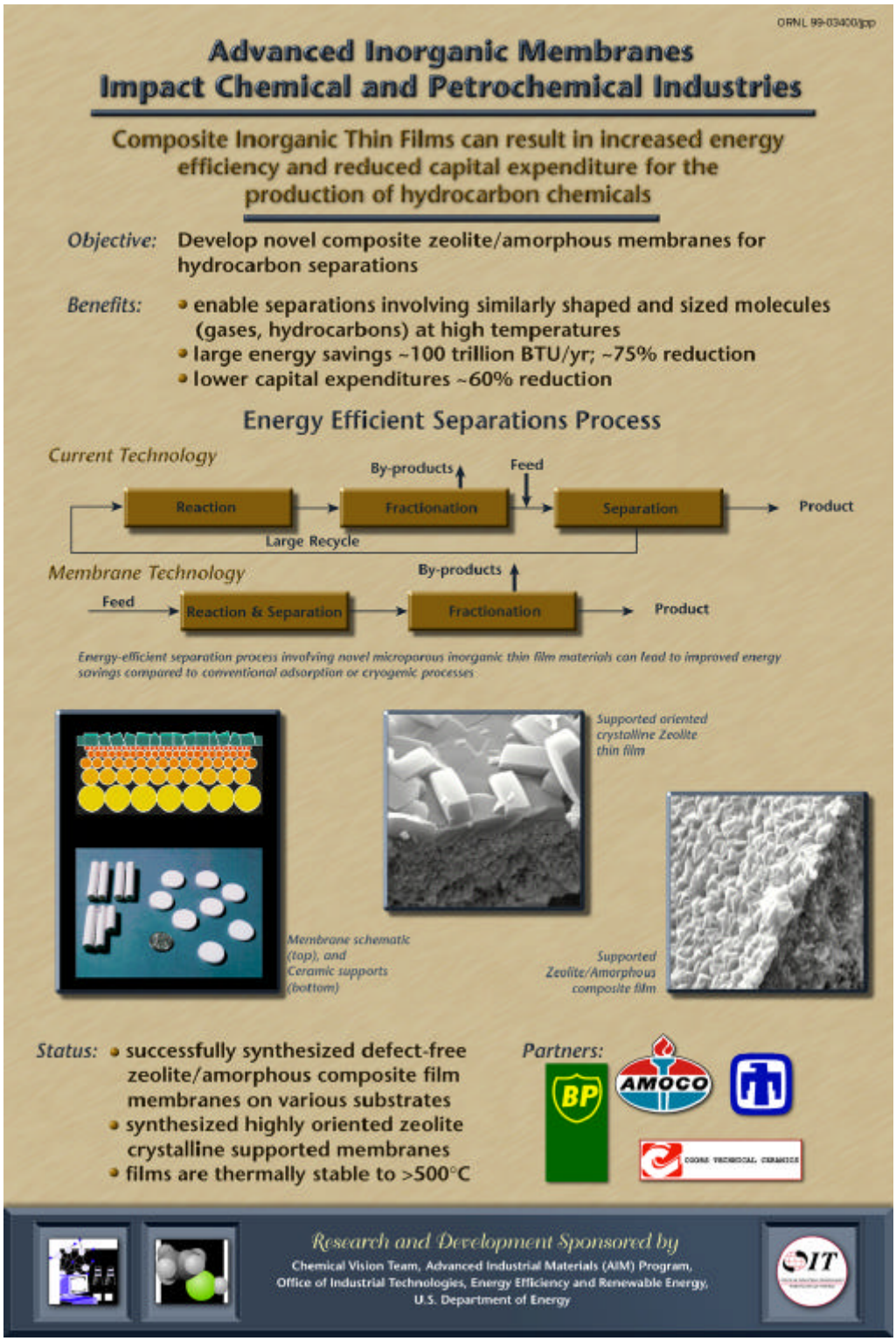
FUTURE PLANS: (1) Transfer funding support and CRADA focus from DOE/AIM to DOE/Vision 2020, which will continue to support the modeling, synthesis or characterization, and industrial scaleup of composite inorganic Zeolite/Sol-gel thin films for hydrocarbon separations. (2) Model the diffusion of binary mixtures of light gases (e.g., H_2, CO_2, H_2O, CH_4, and CH_3OH) and chiral molecules in novel microporous systems and then synthesize and validate the designs in the production of thin, leak-free membranes containing microporous, phosphate-based phases. (3) Develop amorphous hybrid organic-inorganic molecular sieving membranes for gas purification and hydrogen recovery.

POTENTIAL PAYOFF: The petroleum and natural gas refining industries would significantly benefit from high-permeability molecular sieve films capable of separating light, fixed gases, particularly if the membranes can be used at high temperatures. The alkali metal zinc phosphates that we have synthesized as membranes are stable up to 700°C, which is compatible with hydrogen recovery. With sufficiently high permeability and low unit-area cost, energy savings of several quad/year could be achieved when all feasible applications of inorganic membranes are considered.

We currently are developing partnerships with the Amoco Petroleum Division to develop the light-gas media and membranes further (ongoing discussions with Dr. Carl Udovich, Amoco Exploration and Production). Also, we have ongoing discussions with the DuPont Company to develop porous membranes for chiral molecule separations (pertaining to both the pharmaceutical and agrochemical sectors).

SIGNIFICANT ACCOMPLISHMENT

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM



POLYMERS

PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT TITLE: Polymer Electrolyte Electrochemical Reactors of Lowered Energy Consumption

PHASE: FY 1997 **COMPLETION DATE:**

PERFORMING ORGANIZATION: Los Alamos National Laboratory

PRINCIPAL INVESTIGATOR: Shimshon Gottesfeld (505-667-0853)

PHASE OBJECTIVES: Reach stable performance for at least 1 week with chlor-alkali electrochemical reactor (ECR) employing an oxygen cathode and exhibiting cell voltage lower by at least 30% that of present-day industrial chlor-alkali ECR at a current density of 300 A/ft^2. Alternatively, achieve higher throughput (as high as 1000 A/ft^2), while maintaining a significant fraction of this energy savings.

ULTIMATE OBJECTIVES: Optimize materials for the promising new cell design that will fulfill the combined requirements of mechanical and chemical stability in the context of industrial-sized cells. Develop and test ECR, employing such materials/structures, for the chlor-alkali industry, based on an oxygen or air electrode, and demonstrating energy consumption that is 30% lower than that of present-day industrial chlor-alkali ECR at same product throughput and at >90%.current efficiency.

TECHNICAL APPROACH: Novel ECR configuration, based on effective oxygen cathodes developed at LANL, is assembled and tested at LANL. Optimization is based on detailed analysis of losses in the cell and on modification of cell materials and elements following identification of sources of loss. Collaboration with Dow Chemical ensures meaningful comparison with present-day technology. Materials examination regarding mechanical- and corrosion-susceptibility characteristics is performed under the most relevant, well-defined conditions, employing both electrochemical and other analytical techniques.

PROGRESS: A new cell configuration* introduced by us in the fall of 1998 has provided high performance and performance stability of a chlor-alkali ECR with oxygen cathode due to significantly lower and more stable cell resistance. As a result, the following stable cell performance points were recorded: 2.2 V at 400 A/ft^2, 2.45 V at 600 A/ft^2, and 2.7 V at 800 A/ft^2. These results compare with state-of-the-art ECRs in the chlor-alkali industry that operate at 3.2 V at a current density of 300 to 400 A/ft^2.

PROJECT SUMMARY (continued)

PROJECT TITLE: Polymer Electrolyte Electrochemical Reactors of Lowered Energy Consumption

ACCOMPLISHMENTS: *We strongly believe that the most recent results demonstrated by us with the new chlor-alkali ECR based on oxygen cathode are very unique. We are not aware of any comparable achievement in terms of unique ECR structure, high energy savings, and the the possibility of much higher throughput per cell size while maintaining a significant fraction of the energy savings. We are pursuing vigorously patent application.

Publications: 1 **Presentations:** 4 **Disclosures:** 2 **Licenses:** None.

Known Follow-On Products: None. **Industry Workshops:** None.

CRITICAL ISSUES: The most critical issue in this project is demonstration of stable cell performance in operation in the energy-saving mode based on an oxygen cathode. Performance stability depends, in turn, on optimization of cathode structure and cell-operation conditions. The oxygen cathode requires moving away from the materials and flow field employed in the initial ECR demonstration to materials and structures that will provide satisfactory mechanical properties in actual cells several feet high and several feet wide. The natural choice of metallic components from the mechanical perspective will have to be followed by judicious choice of metal components with or without surface treatment that can withstand the caustic environment and the potential of an oxygen cathode.

FUTURE PLANS: Continue to resolve key material and structure issues of the advanced, energy-saving and CO_2-emission-cutting ECR technology developed jointly between LANL and Dow Chemical. Implement such material in testing cells of increasing size at both LANL and Dow Chemical

POTENTIAL PAYOFF: (1) Potential savings of up to 50% of the electrical energy consumed by an industry that uses 2% of the total electrical power generated in the United States. (2) Introduction of new chlor-alkali reactor technology, giving U.S. industry a competitive edge. (3) Cutting CO_2 emissions by up to 50% in an industry that is a major consumer of electricsl power.

ESTIMATED ENERGY SAVINGS: Potential to save up to 50% of the electrical energy consumed by an industry that uses 2% of the total electrical power generated in the United States.

SIGNIFICANT ACCOMPLISHMENT

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

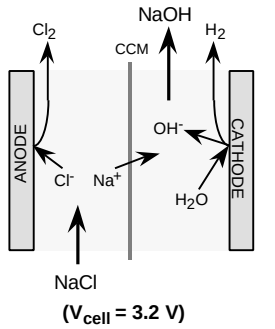
Energy-Efficient Electrochemical Reactors (ECRs)

PROBLEM: The chlor-alkali industry consumes 2% of the total electrical power generated in the United States. The products at the cathode are NaOH and hydrogen gas, and gaseous chlorine is generated at the anode. The cell voltage directly reflects the electrical energy consumption per ton of chlorine (or caustic) product. Lowering of the cell voltage is, therefore, an important energy-savings target for this particular industrial process, as well as for several other industrial processes involving electrochemical oxidations.

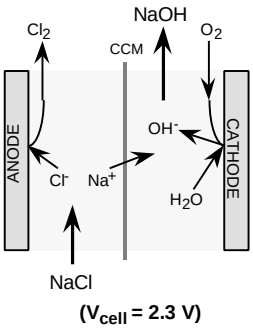
RESULTS: The figure on the left shows the conventional configuration of an ECR used in the chlor-alkali industry, generating chlorine and caustic soda by electrolysis of sodium chloride brine. The cell voltage required at a typical production rate of 300 A/ft^2 is 3.2 to 3.3 V. If the hydrogen-evolving cathode were replaced by an oxygen-consuming cathode (b), the voltage of the cell could be reduced, in principle, by about 0.9 V. In recent years at LANL, we have developed advanced oxygen/air electrodes, and the adaptation of elements of our approach for chlor-alkali ECRs seemed possible. Interest at Dow Chemical resulted in a CRADA agreement between Dow Chemical and LANL that was signed in June 1997. This joint LANL/Dow technical work was augmented in November 1998 with funding from OIT (Chemical Industry), which we committed to enhanced testing and technology-transfer activities. Materials science and technology issues continue to be addressed under the AIM program. A new cell configuration, introduced by us in the fall of 1998, has provided high performance and performance stability of a chlor-alkali ECR with oxygen cathode, due to significantly lower and more stable cell resistance. As a result, the following stable cell-performance points were recorded: 2.2 V at 400 A/ft^2, 2.45 V at 600 A/ft^2, and 2.7 V at 800 A/ft^2. These results compare with those of state-of-the-art ECRs in the chlor-alkali industry that operate at 3.2 V at current density of 300 to 400 A/ft^2.

ENERGY EFFICIENCY: Potential savings of up to 50% of the electrical energy consumed by an industry that uses 2% of the total electrical power generated in the United States plus a lowering of CO_2 emissions.

a) Conventional Chlor-Alkali Cell



b) Chlor-Alkali Cell with Oxygen Cathod



R&D performed at Los Alamos National Laboratory (LANL) under the sponsorship of DOE-EE-OIT, Advanced Industrial Materials Program.

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Mary H. Rawlins