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Inert Anode/Cathode Program

Fiscal Year 1986 Annual Report

June 1987

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On the cover:

Aluminum reduction pots at the Pittsburgh Reduction Company's (Alcoa's) plant in 1889. Adapted from a photograph, courtesy of Alcoa.

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INERT ANODE/CATHODE PROGRAM
FISCAL YEAR 1986 ANNUAL REPORT

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Pacific Northwest Laboratory
Richland, Washington 99352

SUMMARY

This fiscal year 1986 annual report describes the technical achievements of the Inert Anode/Cathode Program. The program is conducted at the Pacific Northwest Laboratory for the U.S. Department of Energy, Office of Industrial Programs.

Major accomplishments and results of the program for the fiscal year are summarized below:

- The electrical conductivity of the Alcoa-developed cermet anode material was increased by a factor of seven by modification of the composition. Initial polarization tests on this new material showed the least amount of wear of all the anode materials tested in FY86. This material will undergo further testing in FY87. The composition of the material will be discussed after the patent disclosure has been filed.
- Polarization studies performed on pure copper suggest that a Cu_2O surface layer is oxidized to CuO during electrolysis. A microstructural examination of copper exposed to cryolite during electrolysis revealed deposits composed mainly of Cu_2O . Copper and aluminate was also identified in the deposits, suggesting that the aluminate was a product of the reaction between an oxide of copper and alumina and/or cryolite. It was previously suggested that copper aluminate was responsible for passivation of copper in the cermet. These results suggest that copper oxides may be important in passivation.
- A spectroscopic cell for in situ laser Raman studies was designed and constructed. It was successfully used to collect Raman spectra of molten cryolite during electrolysis with candidate inert anodes.
- Laboratory research and a literature review were performed to evaluate and recommend prime candidate designs for retrofitting commercial Hall-Heroult cells with TiB_2 -based cathode materials. The most feasible design appears to be use of replaceable TiB_2 -based cathodes that rest unattached on carbon cell bottoms. A second

alternative entails use of replaceable anode/cathode fixtures held in place by inert mechanical spacers. Both approaches require laboratory testing to evaluate long-duration cell performance and material wear mechanisms. Wear-resistant materials, such as TiB_2AlN , high-purity TiB_2 , and TiB_2 -graphite composites are prime candidates for use in these designs.

- Two laboratory cell test systems have been designed and constructed, and are being used to conduct the 20-A Hall-Heroult cell experiments. Baseline aluminum reduction cell tests have been performed on 3-cm-diameter cermet anode materials for periods of 20 and 30 h. The results of these tests will be used to optimize bath chemistry, cell temperature, and operating parameters.
- Short-term wear rates of TiB_2 -graphite cathode materials were measured in a transference cell under electrolytic conditions. Linear extrapolation of the data yielded wear rates calculated for the first year of service of 5 to 26 cm/yr, while parabolic rates were 0.2 to 0.7 cm/yr. Data were collected during relatively short-term tests and fit both linear and parabolic models. Longer tests, of perhaps several hundred hours, would be required to determine which model is appropriate for TiB_2 -G wear under electrolytic conditions.
- Three optical methods for measuring bath liquidus temperature were evaluated; each method was based on a distinctly different approach for detecting the formation of solids in the bath. The techniques, which were based on use of a radiometer, analysis of the spectral energy distribution, and infrared imaging, were used to detect the formation of solids in a cooled portion of the cryolite bath. The bath composition can be determined from the liquidus temperature. Future work will establish the relative accuracy, adaptability to multiplexing, and information pertinent to cost per cell installation for each temperature-measuring method.

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INTRODUCTION

The Inert Anode/Cathode Program is being conducted by the Pacific Northwest Laboratory (PNL) for the U.S. Department of Energy (DOE), Office of Industrial Programs (OIP). The purpose of the program is to develop long-lasting, energy-efficient anodes, cathodes, and ancillary equipment for Hall-Heroult cells used by the aluminum industry. The program is divided into four tasks with the following objectives:

- Inert Anode Development - to improve the energy efficiency of Hall-Heroult cells by development of inert anodes.
- Cathode Materials Evaluation - to confirm the chemical behavior of carbon-containing TiB_2 cathode materials in the presence of molten cryolite and aluminum and to upgrade the analytical procedures for Al_4C_3 in cryolite.
- Cathode Bonding Development - to develop methods for retrofitting Hall-Heroult cells with TiB_2 -based cathode materials.
- Sensor Development - to devise sensors to control the chemistry of Hall-Heroult cells using stable anodes and cathodes.

This Inert Anode/Cathode Program annual report highlights the major FY86 technical accomplishments. The accomplishments are presented in the following sections: Management, Materials Development, Materials Evaluation, Thermodynamic Evaluation, Laboratory Cell Tests, Large-Scale Tests, Cathode Materials Evaluation, Cathode Bonding Development, and Sensor Development.

MANAGEMENT

P. E. Hart

During FY86, additions to the program staff resulted in a strong team to accomplish our program objectives: the development of inert anodes, stable cathodes, and sensors for Hall-Heroult aluminum reduction cells. A major Department of Energy (DOE) milestone was met on the Cathode Materials Evaluation task and several important technical advances were made on the programs. Management activities are discussed in this section of the report, while technical advances are discussed in the following sections.

During the year two new staff members, Bernie Wrona and Chris Schilling, were hired to work on the program. Bernie is the manager of the Laboratory Cell Tests and Large-Scale Tests tasks, while Chris is the manager of the Cathode Bonding Development task. In addition, Steve Marschman was assigned manager of the Materials Development task, while Chuck Windisch became the manager of the Materials Evaluation task. Pat Hart became the program manager and Jim Divine was assigned the responsibility of program technical manager.

With the completion of the major milestone to measure the wear rate of $\text{Ti8}_2\text{-G}$ cathode materials in cryolite under electrolytic conditions, the Cathode Materials Evaluation was completed. Due to restricted funding and higher priorities, the Large-Scale Tests task will not be funded in FY87. Further work on the development of large self-heated test cells will be postponed until FY88.

During FY86, the following reports were issued on the program:

- Wang, R., and S. C. Marschman. 1986. Material Development for Inert Anodes: Progress Report for the Period from May to October 1985. Limited distribution, Pacific Northwest Laboratory, Richland, Washington.
- Windisch, C. F., Jr. and D. I. Boget. 1986. Development of a Standard Bench-Scale Cell for Electrochemical Studies on Inert Anodes. PNL-5898, Pacific Northwest Laboratory, Richland, Washington.

The following reports, which discuss work accomplished in FY86, will be published in FY87:

- Windisch, C. F., Jr. and S. C. Marschman. 1986. Electrochemical Polarization Studies on Cu and Cu-Containing Cermet Anodes for the Aluminum Industry. PNL-SA-14299, Pacific Northwest Laboratory, Richland, Washington.
- Pool, K. H., J. L. Brimhall, P. J. Raney, and P. E. Hart. 1987. Evaluation of Wear Rates and Mechanisms of Titanium Diboride-Graphite Composite Materials Proposed for Use as Cathodes in Hall-Heroult Cells. PNL-6069, Pacific Northwest Laboratory, Richland, Washington.
- Schilling, C. H., D. I. Hagen, and P. E. Hart. Stable Attachment of TiB₂ Based Cathodes for the Aluminum Industry: Review and Recommendation. PNL-6144, Pacific Northwest Laboratory, Richland, Washington.
- Marschman, S. C., and N. C. Davis. Materials Development for Inert Anodes: Progress Report for the Period from October 1985 to January 1987.
- Marschman, S. C., N. C. Davis, and R. W. Stephens. Development of Brazed Electrical Contacts Between Cermets and Metals.

During the year, the program was reviewed and technical interchanges were held with members of staff from the Aluminum Company of America (Alcoa), Eltech Systems Corp., Kaiser Aluminum and Chemical Corp., National Southwire Aluminum Company, Comalco Ltd., Alcan International, Reynolds Metals, Massachusetts Institute of Technology, Great Lakes Research Corp., and the Bonneville Power Administration (BPA). PNL staff participated in a DOE and industry-sponsored review of aluminum reduction programs. In addition, program staff members toured the Kaiser reduction plant located in Mead, Washington, and the Kaiser Research Center in Pleasanton, California.

Program consultants Rudy Keller, Warren Haupin, and Jim Evans reviewed program activities throughout the year. In addition, Keller and Haupin prepared an estimate of the energy savings resulting from the introduction of inert anodes and stable cathodes into reduction cells.

An agreement was reached to provide Eltech Systems Corp. with copper ferrite anode materials, produced at the Pacific Northwest Laboratory (PNL), for evaluation as substrates for coatings. Eltech is evaluating coatings under separate DOE funding. An agreement was reached to supply inert anode materials to Rudy Keller of EMEC Corp. to be used on a National Aeronautics and Space Administration Small Business Innovation Research project to evaluate the dry extraction of silicon and aluminum from lunar ores.

At PNL, a program library with a computerized index and cross reference system was established, containing more than 350 entries. Topics in the library include anode materials, cathode materials, sensors, and aluminum reduction technology.

During the year, suppliers of TiB_2 -based materials were contacted and in several instances these organizations supplied PNL with TiB_2 materials for evaluation as cathode materials.

At the request of DOE-HQ staff, proposals relevant to the development of inert anodes and stable cathodes submitted to DOE were reviewed by PNL staff. In addition, the final report on the Alcoa anode development program was reviewed by PNL staff.

Discussions were initiated with BPA staff regarding the potential for program support during FY87. Proposals relevant to aluminum reduction will be submitted to BPA in FY87.

MATERIALS DEVELOPMENT

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SUMMARY

The objectives of the Materials Development subtask include the selection, fabrication, and evaluation of candidate inert anode materials. Research was performed at PNL in FY86 to develop and evaluate electrically conductive but corrosion-resistant cermet materials.

Research focused primarily on cermets composed of a two-phase oxide system, $\text{NiO-NiFe}_2\text{O}_4$, and a third, electrically conductive, metal phase of copper and nickel. Through fabrication developments and electrolysis testing, four types of cermets based on the $\text{NiO-NiFe}_2\text{O}_4$ system have been identified as materials showing promise as candidate inert anode materials.

- $\text{NiO-NiFe}_2\text{O}_4$ -Cu cermets containing 17 wt% copper--These cermets have been sintered to high densities, and have microstructures with well distributed copper metal phases.
- $\text{NiO-NiFe}_2\text{O}_4$ -Cu-Ni cermets containing 3- to 5-wt% added nickel--These cermets have high electrical conductivity and the ability to passivate during electrolysis.
- $\text{NiO-NiFe}_2\text{O}_4$ -Cu cermets fabricated from freeze-dried powders--These cermets have microstructures showing a fine dispersion of the copper metal phase; they are expected to have conductivity and corrosion properties similar to other copper cermets.
- Reaction-sintered $\text{NiO-NiFe}_2\text{O}_4$ -Cu-Ni-X cermets--These cermets have a copper metal phase that is continuous and passivating.

The $\text{NiO-NiFe}_2\text{O}_4$ -Cu-Ni-X cermets, which performed well in short-term electrochemical screening tests and have exceptional electrical conductivity properties, may be the most promising cermets developed in FY86.

Limited evaluation of powder metallurgically prepared metal alloys was also conducted but the alloys severely corroded in short-term testing. It

appears unlikely that a metal composition could be identified that would satisfy the requirements of an "inert" anode material.

TECHNICAL PROGRESS

Development of materials for use as inert anodes in the electrolytic production of aluminum has been ongoing since the inception of the aluminum industry. Developing materials that can survive the highly corrosive attack of molten cryolite electrolytes has been a difficult problem. Past research into possible anode materials has shown that few materials are resistant to the attack of molten cryolite.

One material that is capable of withstanding the corrosive attack of molten cryolite for prolonged amounts of time is a $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermet (designated 5324 Cu) developed by Alcoa. This cermet is produced by mixing 83-wt% 5324 powder (51.7-wt% NiO , 48.3-wt% Fe_2O_3) with 17-wt% copper powder. The mixture is pressed into shapes, then sintered at 1300°C under an argon atmosphere.

The resulting material consists of three phases: a $\text{Ni}_y\text{Fe}_{1-y}\text{O}$ phase, a NiFe_2O_4 phase, and a Cu-Ni-Fe metal alloy phase. The metal phase is discontinuous throughout the matrix, but is the major electric current-carrying phase within the system, as the oxide phases are known to be poor conductors of electricity. The NiO and NiFe_2O_4 phases provide a corrosion-resistant medium to contain the copper metal phase. This $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermet has an electrical conductivity of approximately $90 \text{ ohm}^{-1}\text{cm}^{-1}$, which is slightly less than one-half the value of the carbon anodes the material is intended to replace. A photomicrograph of the Alcoa-prepared 5324 Cu cermet is shown in Figure 1. Fabrication techniques for producing $\text{NiO-NiFe}_2\text{O}_4$ -based cermets are described in detail below.

Materials Fabrication

The fabrication techniques required to produce the $\text{NiO-NiFe}_2\text{O}_4\text{-metal}$ cermets described in the summary were developed primarily during FY86.

FIGURE 1. Photomicrograph of the Alcoa-Prepared $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ (5324 17-wt% copper) Cermet Material. This sample was sintered at 1300°C in an argon atmosphere.

Fabrication of ceramic or cermet bodies entails several steps. Typically, powders are mixed, formed into shapes called green bodies, and then fired to produce a high-density cermet body.

The procedure developed for the fabrication of $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermet anodes is summarized below. Some samples were prepared using variations of this procedure, and these are discussed where appropriate.

1. Weigh and combine $\text{NiO-NiFe}_2\text{O}_4$ and copper metal powders.
2. Blend powders in the Impandex Inc. Turbula blender.
3. Pre-press samples at low pressure to consolidate the powders.
4. Isostatically press at 25 ksi (172 MPa) in thin rubber containers.
5. Machine green bodies to shape (if required).
6. Sinter samples.

The development of fabrication procedures included powder analysis, blending procedures, pressing procedures, the assembly of a sintering furnace

and associated gas train, and development of a sintering schedule. These tasks, which were accomplished during FY86, are summarized below.

Powder Analysis

The $\text{NiO-NiFe}_2\text{O}_4$ powder was supplied by the Stackpole Corporation. Although Alcoa developed this composition and preliminary powder production techniques, they contracted the Stackpole Corporation to develop a commercial production technique. The exact powder production technique is considered proprietary by the Stackpole Corporation, but much information is contained in a report published by Alcoa (Weyand et al. 1986) pertaining to powder production techniques. The method recommended by Alcoa for producing the $\text{NiO-NiFe}_2\text{O}_4$ powder is summarized below.

The $\text{NiO-NiFe}_2\text{O}_4$ powder used in this study consists of 30-mol% Fe_2O_3 , and 70-mol% NiO (48.3-wt% Fe_2O_3 , 51.7-wt% NiO). This powder is produced by blending the appropriate amounts of Fe_2O_3 and NiO , followed by milling and calcining at 900°C . Apparently, the powder is then milled with a liquid binder. This mixture is then fed to a spray drier where it is spray-dried to spherical powder granules.

Copper powder was obtained by PNL from two sources: Aremco Products Inc. and Cerac Inc. The Aremco copper powder was 99.9% pure. Aremco reported that its copper powder had an average particle size of 1 to 5 μm . Micrographs obtained from the scanning electron microscope (SEM) indicated that the Aremco powder had a size distribution ranging from 5 to 50 μm . Cerac reported an average copper particle size of 2 μm . The average Cerac copper particle size was determined to be 2.4 μm , by sedimentation, and 3.13 μm , by laser diffraction. The largest particle size, as determined from SEM micrographs, was 6.0 μm .

Nickel metal powder was added to some compositions to produce a $\text{NiO-NiFe}_2\text{O}_4\text{-Cu-Ni}$ cermet which had a higher electrical conductivity than the $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermet. The nickel was a 3- μm powder obtained from Aremco; the particle size was not verified.

Additional samples were fabricated using freeze-dried copper powder and freeze-dried $\text{NiO-NiFe}_2\text{O}_4$ powder. The freeze-dried powders were prepared by

pumping salt solutions through an orifice into a bath of hexane which flash-froze the solution into beads. The water was removed in a freeze-drying unit and the powder was calcined to form the desired oxides and metals. A salt solution of CuSO_4 was used to produce the copper metal powder. A salt solution of FeSO_4 and NiSO_4 was used to produce the $\text{NiO-NiFe}_2\text{O}_4$ powder. The resulting sulfate particles were dried in a commercial freeze drier to produce sulfate agglomerates. These agglomerates, or beads, were then heated to the decomposition temperature. The powder may be processed at this point as an oxide or it may be reduced to a highly sinterable metal powder. Freeze-dried powders have extremely small particle sizes, have relatively low bulk densities, and may be easily sintered to high densities at low temperatures.

As mentioned above, the freeze-dried copper powder was prepared from a CuSO_4 solution, and the $\text{NiO-NiFe}_2\text{O}_4$ oxide powder was prepared from a solution of FeSO_4 and NiSO_4 . The required ratio of NiSO_4 to FeSO_4 was calculated from the amounts of NiO and Fe_2O_3 (51.7-wt% NiO , 48.3-wt% Fe_2O_3) used to produce the $\text{NiO-NiFe}_2\text{O}_4$ powder by spray drying. The mixture of FeSO_4 and NiSO_4 was flash frozen at approximately -60°C in hexane, then processed in a freeze drier. The sulfate powder was then calcined at approximately 800°C in air to decompose the sulfate to the oxides NiO and NiFe_2O_4 . This powder was analyzed using x-ray diffraction and was compared to the Stackpole $\text{NiO-NiFe}_2\text{O}_4$ powder. Figure 2 shows the diffraction pattern obtained from the freeze dried $\text{NiO-NiFe}_2\text{O}_4$ powder. Figure 3 shows the diffraction pattern of the freeze-dried $\text{NiO-NiFe}_2\text{O}_4$ powder superimposed on the diffraction pattern of the Stackpole $\text{NiO-NiFe}_2\text{O}_4$ powder. These patterns are nearly identical, differing only in that the PNL freeze-dried $\text{NiO-NiFe}_2\text{O}_4$ powder shows slightly sharper lines in the diffraction pattern. From this analysis, it was concluded that $\text{NiO-NiFe}_2\text{O}_4$ oxide powder could be produced using freeze drying techniques, and that this oxide powder is apparently identical in structure to the Stackpole 5324 powder.

Blending Procedures

Powder preparation techniques were investigated as a means of improving powder reactivity and reducing powder particle size. High-energy vibratory milling was the primary method used to reduce the particle size. In many cases, vibratory milling was also used to blend the powders prior to pressing

FIGURE 2. X-Ray Diffraction Pattern of the Freeze-Dried NiO-NiFe₂O₄ Powder Prepared at PNL

FIGURE 3. Comparison of the X-Ray Diffraction Patterns of the Stackpole NiO-NiFe₂O₄ Powder (5324) and the PNL-prepared NiO-NiFe₂O₄ Powder. The PNL-prepared NiO-NiFe₂O₄ powder is identical except for an increase in the sharpness of the diffraction peaks.

into green bodies. The vibratory milling machine was supplied by Pilamec Limited. In the cases where powders were not vibratory milled, or only one of the components was vibratory milled ($\text{NiO-NiFe}_2\text{O}_4$ powder, for instance), the powders were blended using a Turbula Shaker-Mixer supplied by Impandex, Inc.

Pressing Procedures

Most of the $\text{NiO-NiFe}_2\text{O}_4$ -based cermet samples prepared during FY86 were isostatically pressed at 25 ksi (172 MPa) at room temperature, often being preformed at lower pressures in a hydraulic press. The resulting green bodies had sufficient strength to be machined prior to sintering using common machine tools. The densities of many of the pressed green bodies were determined by weight and dimensions prior to sintering for comparison to post-sintering densities, determined by water immersion.

Sintering Apparatus

The sintering apparatus developed at PNL is the result of extensive experimentation. A schematic representation of the apparatus is shown in Figure 4.

FIGURE 4. Schematic Diagram of the Sintering Apparatus Used at PNL to Sinter Green Cermet Materials

A platinum-wound resistance furnace is equipped with a closed Al_2O_3 muffle which is plumbed with gas fittings and a thermocouple access port. The furnace has a 10-cm-long constant temperature zone rated at 1350°C . The furnace will accept a sample as large as 6.5 cm in diameter. Argon and air flowing through the gas train are metered by two flow meters, mixed using a simple "T" fitting, and analyzed by an oxygen analyzer to monitor the oxygen level of the gas. The gas flows through the furnace which is maintained at a slight positive pressure. A chromel-alumel thermocouple is used to monitor the sintering temperature. The furnace is controlled by a Research Instruments Inc. programmable furnace controller. This controller offers proportional, differential, and integral control of the furnace for accurate temperature control to within $\pm 5^\circ\text{C}$. The system is programmable, which allows ramping of the furnace temperature to conform to any heating schedule.

Sintering Schedule

Many variations in sintering temperature, sintering time, and sintering atmosphere were tried. Samples of $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermets were sintered at temperatures ranging from 1150 to 1350°C . Sintered densities of 6.0 to 6.15 g/cm^3 were obtained at these temperatures. An example of a $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermet sintered at 1150°C is shown in Figure 5. An example of a $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermet sintered at 1300°C is shown in Figure 6. Both of these cermets were fabricated using the Aremco copper powder. The microstructures of the two materials are similar; however, the sample sintered at 1300°C shows slightly larger NiO and NiFe_2O_4 grains than the sample sintered at 1150°C . The copper metal phase particle size is also more uniform.

Samples were sintered at higher temperatures (1300°C as compared to 1150°C) to reduce sintering time. Sintering for short time periods was possible, but, to encourage uniform grain growth and prevent changes in microstructure during anode life, longer sintering times at the higher temperature were necessary. Thus, the $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermets currently produced at PNL are sintered for 8 h at 1300°C .

Experiments were performed to determine the effect of the sintering atmosphere on the behavior of the cermets. It was determined that the atmosphere should be relatively inert. An atmosphere of flowing argon gas containing 100

FIGURE 5. Micrograph of the NiO-NiFe₂O₄-Cu Cermet Material Prepared From the Stackpole NiO-NiFe₂O₄ Powder (5324), and 17-wt% Aremco Copper Powder

FIGURE 6. Micrograph of NiO-NiFe₂O₄-Cu Cermet Material Prepared From the Stackpole NiO-NiFe₂O₄ Powder (5324), and 17-wt% Aremco Copper Powder Sintered at 1150°C

to 200 ppm O_2 was found to work well. This atmosphere contains enough O_2 to keep the NiO and $NiFe_2O_4$ oxides from reducing, and yet is sufficiently low in O_2 to keep the Cu metal phase from oxidizing. Experiments performed using sintering atmospheres with less than 100 ppm O_2 were found to reduce the surfaces of the samples to a nickel-based alloy which would corrode in an electrolysis cell. Thus, 100 ppm O_2 became the minimum level allowed in the sintering furnace.

The sintering schedule developed for fabricating the $NiO-NiFe_2O_4-Cu$ cermet anodes is as follows:

1. Heat from 20 to 650°C in 8 h.
2. Heat from 650 to 1070°C in 6 h.
3. Hold 2 h at 1070°C.
4. Heat from 1070 to 1300°C in 4 h.
5. Hold 8 h at 1300°C.
6. Furnace cool to room temperature.

Cermet Fabrication

In seeking a more conductive but still corrosion-resistant cermet material, several different metal powder additions to the $NiO-NiFe_2O_4$ base were tested. These additions included: copper powder of different particle sizes, nickel powder, freeze-dried and spray-dried powders, and other powders.

$NiO-NiFe_2O_4-Cu$ Cermet Material

Two variations of the $NiO-NiFe_2O_4-Cu$ cermet were produced at PNL during FY86 and exhibited microstructures that appeared to be improvements over the Alcoa material. One variation used an Aremco copper powder with an average powder particle size of 5 to 50 μm , as verified by SEM micrographs; see Figure 7. The second cermet's copper powder was supplied by Cerac, Inc. and contained particles averaging 2.4 μm , with some particles up to 6 μm identified by SEM micrographs; see Figure 8.

Microstructures of the fabricated anode materials are shown in Figures 5 and 9. The anode material prepared using the Aremco copper powder has a microstructure similar to the Alcoa-prepared 5324 copper cermet. The anode sample prepared with the Cerac copper powder has a more uniform distribution of

FIGURE 7. SEM Micrograph of the Aremco Copper Powder

FIGURE 8. SEM Micrograph of the Cerac Copper Powder

FIGURE 9. Micrograph of the NiO-NiFe₂O₄-Cu Cermet Material Prepared from the Stackpole NiO-NiFe₂O₄ Powder (5324), and 17-wt% Cerac Copper Powder

smaller metal particles, which improves the electrical conductivity of this material. While electrical conductivities of the Alcoa-prepared 5324 copper cermet and the PNL-prepared NiO-NiFe₂O₄-Cu cermet (Aremco copper) specimens were measured at PNL to be $64 \text{ ohm}^{-1}\text{cm}^{-1}$ at 950°C , the PNL NiO-NiFe₂O₄-Cu cermet made with Cerac copper powder was measured to be $73 \text{ ohm}^{-1}\text{cm}^{-1}$ at 950°C . This 13% improvement in the conductivity is due to the improved distribution of the copper metal phase in the Cerac copper NiO-NiFe₂O₄-Cu cermet material.

Another advantage of the Cerac copper powder, as used in our experiments, was the ability to prepare samples that contained higher copper loadings. The NiO-NiFe₂O₄-Cu cermet produced by Alcoa and the NiO-NiFe₂O₄-Cu cermets produced at PNL using the Aremco copper powder contained 17-wt% copper before sintering. Copper levels higher than 17 wt% resulted in metal phase bleedout during sintering. Using the finer copper powders, copper levels as high as 20 wt% have been obtained without metal phase bleedout during sintering. Higher copper

loadings increase the electrical conductivity, while maintaining a good microstructure. These improvements may justify the increase in cost inherent to very fine powders, if corrosion resistance is sufficient.

Electrochemical screening tests were used to test the compatibility of these cermets in molten cryolite under electrolysis conditions. Both materials performed well, with little or no apparent wear or corrosion during electrolysis testing at 1 A/cm^2 at 960°C in electrolytes with a bath ratio of 1.07. No corrosion currents were detected for either of these cermet materials during dc polarization studies.

Fabrication of $\text{NiO-NiFe}_2\text{O}_4\text{-Cu-Ni}$ Cermets

Analysis of $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermets using SEM, coupled with quantitative energy dispersive analysis of x-rays (EDAX), showed that the metal phase present in the cermet was composed of approximately 85-wt% copper and 15-wt% nickel. It was initially believed that the process of nickel diffusion into the copper metal phase was controlled by solid-state diffusion processes between the excess NiO and copper metal. If this diffusional process achieved equilibrium during sintering, then cermets could be prepared using a prealloyed Cu-Ni metal powder. The resulting cermets would not be depleted in NiO , and might produce materials that would exhibit improved corrosion properties. Other possible benefits of adding nickel prior to sintering might include improved sinterability and a more finely dispersed metal phase in the final sintered product to improve conductivity.

Cermets were prepared that contained 1- to 5-wt% nickel prior to sintering. It was observed that the overall metal content (and copper-metal content) of the cermet samples could be increased by adding nickel. A minimum of 3-wt% nickel was necessary to increase the copper-metal content above the 17-wt% bleedout limit found for $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermets. Amounts of less than 3-wt% nickel resulted in the fabrication of cermets that experienced significant metal phase bleedout during sintering. Additions of 3- to 5-wt% nickel resulted in cermets that could contain as much as 21-wt% copper prior to sintering. Nickel metal contents of more than 5 wt% did not show any additional improvements. The maximum metal content that was achieved using this technique was 25 wt% (20-wt% copper and 5-wt% nickel).

The $\text{NiO-NiFe}_2\text{O}_4\text{-Cu-Ni}$ cermets were fabricated using procedures almost identical to the $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermets discussed above. The nickel powder was blended with the $\text{NiO-NiFe}_2\text{O}_4$ and copper powders during the blending step. The nickel powder was obtained from the Aremco Company with a reported particle size of $3\text{ }\mu\text{m}$. A typical microstructure for the $\text{NiO-NiFe}_2\text{O}_4\text{-Cu-Ni}$ cermets is shown in Figure 10. The metal phase is discontinuous, but the measured electrical conductivities for these materials are 2.5 times greater than for the $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermets without nickel additions.

Electrochemical screening tests performed on the $\text{NiO-NiFe}_2\text{O}_4\text{-Cu-Ni}$ cermets have been promising. In short-term tests, these cermets have shown little wear or corrosion. The dc polarization sweeps performed on these materials have not detected the presence of corrosion currents. These studies have also indicated that the materials are protected by a passivation mechanism. These results and other analytical testing results are discussed in a later section.

FIGURE 10. Micrograph of the $\text{NiO-NiFe}_2\text{O}_4\text{-Cu-Ni}$ Cermet Material Prepared from the Stackpole $\text{NiO-NiFe}_2\text{O}_4$ Powder (5324), 20-wt% Ceriac Copper Powder, and 5-wt% Aremco Nickel Powder

Fabrication of NiO-NiFe₂O₄-Cu Cermets Using Freeze-Dried Powders

Metal phase distribution improvements in NiO-NiFe₂O₄-based cermets have been made by utilizing freeze-drying technology. Freeze drying produces powder with smaller particle sizes which, in turn, leads to cermets with a more refined microstructure.

Freeze-dried powders are known to be highly reactive; they will sinter to higher densities at lower temperatures than powders prepared by other techniques. NiO-NiFe₂O₄-Cu cermets produced using spray-dried NiO-NiFe₂O₄ powder and freeze-dried copper powder were sintered to a density 10% higher than NiO-NiFe₂O₄-Cu cermets prepared from spray-dried NiO-NiFe₂O₄ powder and the larger Areemco copper powder (6.07 g/cm³ versus 5.99 g/cm³). These were sintered for 3 h at 1100°C. A photomicrograph of a NiO-NiFe₂O₄-Cu cermet fabricated from spray-dried NiO-NiFe₂O₄ powder and freeze-dried copper powder is shown in Figure 11. The use of freeze-dried copper powder also increased the amount of copper metal that could be added to the cermet. The sample shown in Figure 11

FIGURE 11. Micrograph of the NiO-NiFe₂O₄-Cu Cermet Material Prepared from the Stackpole NiO-NiFe₂O₄ Powder (5324), and 20 wt% PNL-Prepared Freeze-Dried Copper Powder

contained 20 wt% copper prior to sintering. This cermet did not exhibit any metal phase bleedout during sintering. The benefit of increased copper metal content is greater electrical conductivity.

Cermets were also prepared from freeze-dried $\text{NiO-NiFe}_2\text{O}_4$ and freeze-dried copper powder. It was determined that these cermets could be sintered to a high density at a lower temperature than cermets fabricated from powders produced by spray drying and other methods. The sample shown in Figure 12 was sintered at a temperature of 1000°C to a density of 6.00 g/cm^3 . Two benefits of low temperature sintering are energy savings during fabrication and fabrication using a solid state sintering process. Sintering above the melting point of copper involves liquid phase sintering, which limits the quantity of copper that can be contained in the cermet to around 17 wt%. Lower sintering temperatures have been attempted using non-freeze-dried copper powder (Aremco), but the cermets produced have had poor microstructures and low densities. The

FIGURE 12. Micrograph of the $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ Cermet Material Prepared from the PNL-Prepared Freeze-Dried $\text{NiO-NiFe}_2\text{O}_4$ Powder, and 25-wt% PNL-Prepared Freeze-Dried Copper Powder

cermet shown in Figure 12 contains 25-wt% copper, and did not exhibit any metal phase bleedout during sintering. This increased metal content will benefit the electrical conductivity of the cermet. Due to a limited quantity of freeze-dried copper powder, not enough samples could be fabricated during FY86 to perform a full analysis on this material.

Fabrication of Reaction-Sintered NiO-NiFe₂O₄-Cu-Ni-X Cermets

The fourth NiO-NiFe₂O₄-based cermet produced was a NiO-NiFe₂O₄-Cu-Ni-X cermet using another material to promote a reaction process during sintering. The compositions and fabrication procedures used to produce this cermet are the subject of a patent disclosure and are not discussed in this report. A representative microstructure of this material is shown in Figure 13. The porosity of the sample is a result of the additional material added to the cermet and the processing procedure. Samples had lower densities (5.7 g/cm³) than the unreacted NiO-NiFe₂O₄-Cu cermets (6.1 g/cm³). Electrical conductivity measurements yielded a conductivity of 410 ohm⁻¹cm⁻¹ at 950°C. This is a significant increase over the unreacted NiO-NiFe₂O₄-Cu and NiO-NiFe₂O₄-Cu-Ni cermets. This

FIGURE 13. Micrograph of the Reaction-Sintered NiO-NiFe₂O₄-Cu-Ni-X Cermet Material

increase in electrical conductivity is attributed to the type of electrical conduction that occurs in the cermet. In reaction-sintered materials, the metal phase developed is continuous, which results in the material having the electrical conductivity properties of a metal. The non-reaction-sintered NiO-NiFe₂O₄-Cu cermets have a discontinuous metal phase which produces a material having the electrical conductivity of a semi-conductor.

Electrolysis testing on the reaction-sintered materials has also been promising. Short-term screening tests have shown little corrosion or erosion of the sample. Direct current polarization sweeps have not been performed on this material, as electrical lead wire failures limited testing of the material during FY86. The failures were due to the use of nichrome wire as the lead wire material. This problem was corrected, but time restrictions prohibited further testing of this cermet material in FY86.

Fabrication of Powder Metallurgically Prepared Metals

Research performed during FY85 at PNL indicated that fine grain metal alloys were resistant to the corrosive attack of cryolite during non-polarized static soak tests. These alloys were based on a phase field of the following metals:

Nickel	37 to 65 wt%
Iron	10 to 30 wt%
Copper	3 to 10 wt%
Chromium	0 to 15 wt%
Aluminum	0 to 15 wt%

Various combinations of these metals within this phase field were developed using a statistically designed study. The alloys were prepared using standard powder metallurgical techniques. Powders were obtained from various manufacturers. The powders were mixed in a mechanical blender, pressed at 25 ksi (172 MPa), then sintered at approximately 1200°C in an inert atmosphere. Some of the samples were analyzed for performance in small Hall-Heroult electrolysis cells. The results of those tests are discussed later in this section.

Materials Analysis

Analysis of materials developed at PNL during FY86 involved several techniques. These included optical microscopy, SEM, EDAX, electrical conductivity measurements, and electrolysis testing in small Hall-Heroult cells.

Optical Microscopy

Optical microscopy was used to examine the microstructure of cermets both before and after electrolysis testing. SEM and EDAX were used to examine cermets at higher magnifications than possible with optical microscopy, and also to determine the composition of phases present. SEM was also used to determine powder particle sizes and to investigate the effect of vibratory milling on powders. Electrolysis screening tests were performed in small Hall-Heroult electrolysis cells to determine material compatibility with molten cryolite-based electrolytes under polarized conditions. Additionally, dc polarization sweeps were performed to determine the presence of passivation layers or corrosion currents.

Although the microscopy techniques need no explanation, a review of the techniques used to determine the electrical conductivity of the materials and electrolysis behavior of the materials is necessary as these techniques vary in practice.

Electrical Conductivity Measurements

The apparatus used to determine the electrical conductivity of the cermet samples is illustrated in Figure 14. The apparatus consists of a high temperature furnace and furnace controlling equipment, an alumina tube which is closed at one end, and an assembly head. The assembly head holds the sample and sample contacts at the end of alumina support rods. The assembly head also contains the inert purge gas inlet and exit tubes. Temperature, electrical current, and voltage are measured by dedicated instruments, and power is supplied to the sample by a regulated dc power supply.

Figure 15 illustrates schematically the four-wire conductivity apparatus and the way in which the samples are placed in the apparatus. The sample is held on the ends by two platinum contacts that are used as power leads and thermocouple junctions. These contacts have both platinum and platinum/rhodium

FIGURE 14. Schematic Diagram of the Apparatus Used to Measure the Electrical Conductivity of Fabricated Cermet Materials

leads that make up the thermocouple leads. The platinum leads are also used as the electrical power leads to the sample. Two platinum point contacts are set 2 cm apart on the sample and are used to take the voltage measurements. Current is measured by an ammeter which is in series with the electrical power leads. The electrical conductivity is determined from the voltage, current, cross sectional area of the sample, and the length between the two point contacts used to measure the voltage.

Electrolysis Cell Used for Screening Tests

A small electrolysis cell was developed for use in testing the compatibility of materials in cryolite-based electrolytes under polarized conditions. This cell is pictured in Figure 16. The outer crucible is constructed of type 304 stainless steel. High-density graphite is used to make the cell liners. Alumina crucibles are used to contain the electrolyte. Use of alumina limits experiments to alumina-saturated electrolytes.

The cell lid is fabricated from Inconel® 601 alloy, and contains six holes for access into the crucible. These include holes for a thermocouple, feed tube, reference electrode, gas sparging tube, anode assembly, and a general access tube. The cell can be fed Al_2O_3 with a screw feeder for extended operation.

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FIGURE 16. Small Electrolysis Cell Used for dc Polarization and Materials Screening Tests

The electrolysis cell is externally heated by a resistance-heated furnace. The cell is controlled by one of the following: a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat, a PAR Model 363 potentiostat/galvanostat, or a Hewlett Packard regulated constant voltage, constant current power supply (for high current density operation). The potentiostats are connected to a Hewlett Packard X-Y recorder for recording of dc polarization sweep experiment data. This electrolysis cell is illustrated in Figure 17.

Discussion

Following are more detailed discussions and conclusions on the effect of particle size on cermet characteristics, the electrical conductivity of the cermets, and electrolysis testing of the cermet anodes.

Effect of Powder Particle Size on Cermet Characteristics

Experiments were performed to determine the effect of milling powders on the sinterability and final microstructure of $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermets. Cermets fabricated from powders that had been subjected to vibratory milling were compared to cermets that were fabricated from as-received powders.

FIGURE 17. Diagram of Electrolysis Cell Apparatus

Milling experiments were performed on $\text{NiO-NiFe}_2\text{O}_4$ powder. A Pilamec Limited vibratory milling machine was used to mill samples of spray-dried $\text{NiO-NiFe}_2\text{O}_4$ powder. Figure 18 is an SEM micrograph of $\text{NiO-NiFe}_2\text{O}_4$ powder that has been vibratory milled for 2.5 h with stainless steel milling balls in a Freon® milling solution. Figure 19 shows an SEM micrograph of the as-received spray-dried $\text{NiO-NiFe}_2\text{O}_4$ powder granules. The vibratory milling process breaks down these granules and increases the surface area of the powder. The vibratory milled powder granules were no longer spheroidal, and no agglomerates larger than 45 μm were found. The as-received spray-dried $\text{NiO-NiFe}_2\text{O}_4$ powder contains granules as large as 75 μm , by comparison. Since this as-received spray-dried powder was highly active, little improvement in sinterability was gained by the vibratory milling.

These powders were used to prepare 100-wt% $\text{NiO-NiFe}_2\text{O}_4$ oxide samples as standards in six sintering experiments. The green body and sintered densities

FIGURE 18. SEM Micrograph of the Stackpole $\text{NiO-NiFe}_2\text{O}_4$ (5324) Powder That Was Vibratory Milled for 2.5 h

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FIGURE 19. SEM Micrograph of the As-Received Stackpole NiO-NiFe₂O₄ (5324) Powder

are compared in Table 1. The fineness of the vibratory milled NiO-NiFe₂O₄ powders resulted in slightly better packing, and green body densities about 2% higher than those obtained from the as-received spray-dried NiO-NiFe₂O₄ powder. The sintered densities of the samples from both fabrication methods range from 5.67 to 5.75 g/cm³; these are considered to be essentially the same within measurement error. Alcoa has reported that the theoretical density of NiO-NiFe₂O₄ oxide samples is 5.7 g/cm³, and in actual practice this value may vary due to the reduction of NiO caused by the sintering atmosphere and the binder used in the fabrication of the powder.

Vibratory milling was also used to blend the NiO-NiFe₂O₄ and copper powders. SEM micrographs of these powders are shown in Figures 20 and 21. The copper powder used in both cases was the copper powder obtained from Aremco. Figure 20 illustrates that mechanical blending does not change the morphology of the NiO-NiFe₂O₄ or copper powder in any way. Figure 21 shows that the vibratory milling intimately mixes the powders and creates a powder mixture of similarly shaped particles. Examples of cermets that were fabricated from these powders are shown in Figures 22 and 23. There is no appreciable

TABLE 1. Densities of Sintered and Green NiO-NiFe₂O₄ and NiO-NiFe₂O₄-Cu Powders

Run No.	Sintering Temperature, °C	NiO-NiFe ₂ O ₄ Powder				NiO-NiFe ₂ O ₄ -Cu Powder ^(a)			
		As-Received, Spray-Dried, g/cm ³		Vibratory Milled for 3 h, g/cm ³		Mechanically Blended, g/cm ³		Vibratory Milled for 2.5 h, g/cm ³	
		Green	Sintered	Green	Sintered	Green	Sintered	Green	Sintered
30 ^(b)	1150	3.38	5.72	3.44	5.75	3.66	6.10	3.78	6.14
31	1200	3.39	5.67	3.50	5.71	3.70	6.01	3.87	6.07
32	1175	3.38	5.73	3.48	5.70	3.71	6.09	3.78	6.11 ^(c)
33 ^(b)	1150	3.41	5.69	3.50	5.71	3.61	6.04	3.85	6.08
34	1250	3.43	5.73	3.46	5.73	3.73	6.09	3.97	6.09 ^(c)
35	1250	3.43	5.70	3.44	5.74	3.68	6.07	3.80	6.13 ^(c)

(a) 83 wt% NiO-NiFe₂O₄ and 17 wt% copper.

(b) No metal phase bleedout from any samples during these runs.

(c) Metal phase bleedout from sample.

FIGURE 20. SEM Micrograph of the Stackpole NiO-NiFe₂O₄ (5324) Powder That Was Mechanically Blended with 17-wt% Aremco Copper Powder

FIGURE 21. SEM Micrograph of the Stackpole NiO-NiFe₂O₄ (5324) Powder That Was Vibratory Milled with 17-wt% Aremco Copper Powder

FIGURE 22. Optical Micrograph of a $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ Cermet Prepared from Mechanically Blended Stackpole $\text{NiO-NiFe}_2\text{O}_4$ Powder (5324), and 17-wt% Aremco Copper Powder

FIGURE 23. Optical Micrograph of a $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ Cermet Prepared from Vibratory Milled Stackpole $\text{NiO-NiFe}_2\text{O}_4$ Powder (5324), and 17-wt% Aremco Copper Powder

difference in the microstructures of these two samples; the copper metal phase is distributed throughout the two samples similarly. Table 1 contains data obtained from six sintering experiments used to fabricate these samples. The cermets produced from vibratory milled powders have only a marginally higher sintered density, averaging a 0.5% increase in density.

As noted above, vibratory milling the powders prior to fabrication did not improve the sinterability of the oxide, nor did it sufficiently break up the copper powder to effect any improvement in the distribution of the metal phase. Apparently, the copper is malleable enough to resist breaking up into a finer powder when vibrationally milled with the $\text{NiO-NiFe}_2\text{O}_4$ powder. Thus, the dispersion of copper in the vibrationally milled powders differs little from that of powders that were simply dry blended. These results could be quite different in the case of the small Cerac copper powder. Additional work is indicated in this area to possibly increase the copper metal or alloy content of $\text{NiO-NiFe}_2\text{O}_4$ -Cu-based cermets by vibratory milling.

Electrical Conductivity

Electrical conductivity measurements were made on several cermet samples. The determinations were made at temperatures between 950 and 1040°C. No attempts were made to record electrical conductivity as a function of temperature to determine the type of electrical conductor each material was. It was assumed that all cermets fabricated were semiconducting in nature, unless some type of unusual behavior was detected. This assumption was based on work performed by Alcoa.

Table 2 summarizes the electrical conductivity measurements of cermets fabricated at PNL and at Alcoa. It can be seen from the data in the table that the electrical conductivity values for $\text{NiO-NiFe}_2\text{O}_4$ -Cu cermets fabricated by Alcoa and PNL were similar. The average electrical conductivity value for the $\text{NiO-NiFe}_2\text{O}_4$ -Cu cermets is $60 \text{ ohm}^{-1}\text{cm}^{-1}$. This value is lower than the $90 \text{ ohm}^{-1}\text{cm}^{-1}$ reported by Alcoa for its 5324 copper cermet. The discrepancy most likely lies in the technique used to make the measurements.

TABLE 2. Summary of Electrical Conductivity Measurements Performed on NiO-NiFe₂O₄-Cu-Based Cermets

Material	Electrical Conductivity, (ohm ⁻¹ cm ⁻¹)	Temperature, °C
Alcoa 5324 (17% Cu)	64.0	996
NiO-NiFe ₂ O ₄ -Cu (17% Aremco Cu)	53.4	995
NiO-NiFe ₂ O ₄ -Cu (17% Aremco Cu)	64.0	1040
NiO-NiFe ₂ O ₄ -Cu (17% Aremco Cu)	66.1	1004
NiO-NiFe ₂ O ₄ -Cu (17% Aremco Cu)	55.3	1004
NiO-NiFe ₂ O ₄ -Cu (17% Cerac Cu)	73.3	1006
NiO-NiFe ₂ O ₄ -Cu-Ni (21% Cerac Cu, 4% Aremco Ni)	169.0	1013
NiO-NiFe ₂ O ₄ -Cu-Ni (21% Cerac Cu, 4% Aremco Ni)	172.0	995
NiO-NiFe ₂ O ₄ -Cu-Ni-X (25% Cerac Cu, 3% Aremco Ni, X)	411.0	950

Alcoa reportedly used a slightly different method from that used at PNL for attaching cermet samples to the electrical conductivity apparatus.^(a) The method used by Alcoa involved cutting shallow grooves around the round cermet sample which held platinum wires tied to the sample. These platinum wire ties were coated with platinum paste. Four grooves were cut into the sample, and the distance between the middle two was measured to precisely determine the electrical conductivity. The outside platinum wire ties were used to feed current to the sample and the middle two platinum wire ties were used to measure voltage. A problem may exist with this technique in that the effective cross sectional area of the sample may differ from the measured cross sectional area. This problem would result if the depth of the grooves cut in the sample was not considered in the calculations of cross sectional area.

(a) Personal communication with G. P. Tarcy, October 1986.

The method used at PNL does not involve cutting grooves into the sample. The cermet sample is machined precisely to a rectangular shape, and current is fed to the sample through two point contacts. Two middle point contacts are used to measure the voltage. A small drop of platinum paste is used to enhance the electrical contact of the two middle point contacts. One unlikely problem with the PNL technique could be in establishing a good electrical contact. The small point contacts used could provide a faulty contact even though the platinum paste is used to enhance the contact. However, this technique has been used at PNL for measuring the electrical conductivity of many different types of materials without this type of problem occurring, and it is unlikely that this problem exists in the measurement of these cermets.

These differences between the PNL and Alcoa techniques may be the reason for the difference in electrical conductivity values. However, the values obtained by both laboratories are within reasonable agreement. It can be concluded from the measurements obtained at PNL that the cermets produced at PNL are of similar electrical conductivity to the Alcoa-prepared cermets.

The use of small copper particle sizes in the fabrication was shown to produce a more finely divided copper metal phase in NiO-NiFe₂O₄-Cu cermets. A NiO-NiFe₂O₄-Cu cermet (17-wt% copper) prepared using the Cerac copper powder was presented in Figure 5. The electrical conductivity of this material was measured to be 73.3 ohm⁻¹cm⁻¹ at 1000°C. This is a 13% improvement over the measured value of the Alcoa-prepared cermet, and cermets prepared at PNL using the Aremco copper powder. Although this improvement is significant, the added cost of very fine copper powders may offset the benefits of this improvement.

Two samples of NiO-NiFe₂O₄-Cu-Ni cermets were also tested. The electrical conductivity of these samples was substantially higher than the NiO-NiFe₂O₄-Cu cermets (17 wt% copper). Although the metal phase appears to be discontinuous throughout the cermets, the electrical conductivity values were measured at an average of 170 ohm⁻¹cm⁻¹. This value is about 2.5 times that of the NiO-NiFe₂O₄-Cu cermets (17-wt% copper) produced at PNL and Alcoa. The improvement is attributed to the influence of the added nickel on the metal phase, although the exact mechanism for the significant improvement remains unknown.

The electrical conductivity of a $\text{NiO-NiFe}_2\text{O}_4\text{-Cu-Ni-X}$ reaction-sintered cermet was also determined. The measured value was substantially higher than the other samples measured. A value of $411 \text{ ohm}^{-1}\text{cm}^{-1}$ at 950°C was found for the electrical conductivity of this sample. Apparently, this high value is a direct result of the continuous metal phase developed in this type of cermet. This value is two times that of the present day carbon anodes used in aluminum smelting.

Electrolysis Testing

Electrolysis testing was used to evaluate the behavior of many of the cermets developed at PNL in molten cryolite-based electrolytes under polarized conditions. Cells were typically operated for 6 to 8 h, with several cells operated for longer durations. Each cell was operated between temperatures of 950 and 960°C , using an alumina-saturated electrolyte. The electrolyte had a bath ratio of 1.07, as mixed. The anodes were all operated at a current density of 1.0 A/cm^2 . The cathode current density varied from cell to cell as these tests were often used to test cathode materials as well. The anode-to-cathode distance was 2 cm; most cells were started without the presence of an aluminum pad. An aluminum reference electrode was employed for use in taking dc polarization data. The design of this electrode was taken from a paper by Burgman, Leistra, and Sides (1986). Chromel-alumel thermocouples sheathed in alumina tubes were used to measure the temperature of the cells during operation. A summary of several of the experiments is presented below.

The first electrolysis tests performed on materials concentrated on the Alcoa $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermet and the PNL $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermet which was fabricated using the Aremco copper powder. Both cermets contained 17-wt% copper prior to sintering.

The Alcoa-prepared cermet was polarized galvanostatically for 3 h, using a graphite cathode. The cell was autopsied after cool down, and the anode did not appear corroded or eroded during the experiment. The cell was switched to potentiostatic operation at the end of the experiment and a dc polarization sweep was performed. The resulting voltammogram is shown in Figure 24. The polarization sweep was started from near the open circuit potential of 1.8 V, then the voltage was increased linearly at a rate of 0.01 mV/s to 3 V (forward

FIGURE 24. Voltammogram of the Alcoa-Prepared $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ Cermet Material. The forward trace represents the portion of the polarization sweep made from 1.8 to 3.0 V, and the reverse trace represents the portion from 3.0 to 2.08 V.

trace). The voltage was then decreased at the same rate until open circuit was reached (reverse trace). The break in the forward trace at 2.15 V is the point at which oxygen evolution begins during the electrolysis of Al_2O_3 to aluminum metal.

The difference in the forward and reverse traces may be explained by examination of polarization data available for the constituents present in the anode. Tarcy (1986) reported polarization curves for copper metal anodes. The data presented by Tarcy indicate a small peak at approximately 2.10 V that corresponds to the peak observed in the forward trace of the voltammogram obtained from the Alcoa $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermet anode. This may indicate that the resi-

dual currents found in the forward trace prior to oxygen evolution may be due to corrosion of the copper metal phase. The reverse trace does not exhibit the same residual currents; this behavior is explained by evaluation of the way in which the polarization sweeps are performed.

A $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermet that has been operated at galvanostatic conditions for a period of time is known to passivate (Weyand et al. 1986). This passivation layer is most likely a copper-containing oxide or aluminate which may be reduced back to a copper-containing alloy or copper metal plus an oxide species if the environment becomes reducing in nature. This condition is created when a cell is switched to potentiostatic operation and the voltage is set so that the cell is forced to be at zero current or open circuit potential (OCP). Thus, as the cell is held at OCP prior to a dc polarization sweep, sufficient time exists for the passivation layer to become at least partially reduced. When the polarization sweep is started, the freshly reduced copper immediately oxidizes, and the process is detected by the potentiostat. The reverse trace is relatively devoid of this information as the reduction process is apparently slower than could be detected at the voltage stepping rate used in this experiment.

The above discussion does not explain the presence of the hysteresis which is present between the two curves. This effect was investigated using a PNL-prepared $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermet anode in another experiment. The cell was operated galvanostatically for 4 h, under experimental conditions identical to the Alcoa $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ anode test conditions and to those discussed above. The cell was then switched to potentiostatic operation to perform the dc polarization sweeps. The cell was initially set to operate at a fixed potential of 3 V. This would prevent the reduction of any passivation layers. A dc polarization sweep was performed from 3 V to the OCP (forward trace), and then from the OCP back to 3 V (reverse trace). The resulting voltammogram is shown in Figure 25.

The residual currents are missing from this voltammogram as expected. Some hysteresis is present between the two curves. The curves shown in Figures 24 and 25 have several similarities. The reverse trace in Figure 24 corresponds to the forward trace in Figure 25. These are the portions of the

FIGURE 25. Voltammogram of the PNL-Prepared $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ Cermet Material. The forward trace represents the portion of the polarization sweep made from 3.0 to 2.08 V, and the reverse trace represents the portion from 2.08 to 3.0 V.

sweeps during which reduction of the passivation layer would occur. Both of these traces have similar slopes and intersect the x axis at 2.08 V. The reverse trace in Figure 25 corresponds to the forward trace in Figure 24. These are the portions of the sweeps during which oxidation of the metals present would occur. Although complete polarization curves are not shown in Figures 24 and 25, both curves were found to have an intersection point at 2.6 V. The similarities between the polarization sweeps of these two materials which were performed in different directions may suggest that the hysteresis effects observed are entirely due to the oxidation process of copper metal contained in the anodes.

An electrolysis cell was assembled using a copper metal anode to investigate this theory. The cell was constructed identically to the other cells. The anode was polarized galvanostatically at 1 A/cm^2 for 2 h at 960°C , after which dc polarization experiments were performed on the anode. The dc polarization sweeps were performed at a rate of 1 mV/s , starting from the OCP to 3 V (forward trace), then from 3 V to the OCP (reverse trace). The resulting voltammogram is shown in Figure 26.

FIGURE 26. Voltammogram of a Pure Copper Anode

The forward trace contains two distinct oxidation peaks occurring at 2.16 V and 2.43 V. Hysteresis between the two traces occurred below 2.70 V. The first oxidation peak and the voltage at which the hysteresis occurred correspond to the oxidation peak found during polarization of the NiO-NiFe₂O₄-Cu anodes discussed above. Thus, the residual currents and hysteresis observed in the polarization experiments are attributed entirely to the oxidation/reduction processes of the copper metal phase contained in the cermets. Efforts to identify the exact corrosion processes occurring during the polarization of NiO-NiFe₂O₄-Cu-type cermet materials are discussed in another section of this report.

It is apparent that NiO-NiFe₂O₄-Cu cermets must develop some type of corrosion protection during electrolysis. If these materials did not develop this protection during polarization, then the residual currents detected during the evaluation of the Alcoa-prepared NiO-NiFe₂O₄-Cu cermet would be present no matter which way the dc polarization sweeps were performed. In an attempt to gain knowledge about the protection mechanism generated during electrolysis, the copper anode discussed above was sectioned for metallographic and SEM and EDAX analysis.

Figures 27 and 28 show two magnifications of the copper anode after 3 h of electrolysis. A stratified 270- μ m-thick dark gray reaction layer formed on the surface of the anode that was directly exposed to cryolite. The composition of the reaction layer was determined using quantitative EDAX. While most of the reaction layer is composed of copper oxide, the crystalline structures on the surface of the anode were found to contain copper and aluminum. This may be the copper aluminate layer mentioned in the Alcoa reports. However, because this layer is found on the surface of the copper oxide layer, it is more likely that the passivation layer is actually the copper oxide layer.

Another cell was assembled using a PNL-prepared NiO-NiFe₂O₄-Cu cermet anode. The cell was operated for 8 h at 950°C at an anode current density of 1 A/cm². The cell was disassembled and autopsied at the end of the experiment. Microstructures of the anode are shown in Figures 29 and 30. The cracks which are visible in Figure 29 are believed to have occurred during cooldown of the cell. Figure 30 shows the surface that was exposed to the electrolyte during

FIGURE 27. Section of a Copper Metal Anode After 3 h of Galvanostatic Polarization at 1 A/cm^2 Anode Current Density

the experiment. The reaction layer averaged $30 \text{ } \mu\text{m}$, and the surface was depleted of the metal phase. An increase in the internal porosity of the cermet is also apparent (as compared to the as-fabricated cermets shown in Figures 5 and 9). Weyand et al. (1986) have suggested that this porosity may be due to oxidation of the metal phase during electrolysis. They did not report what mechanism would be responsible for this oxidation.

The increase in porosity was investigated using SEM. SEM micrographs of the $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermet polarized for 8 h are shown in Figures 31 and 32. The increase in porosity occurs along grain boundaries. The micrograph in Figure 32 shows that the individual grains are apparently reducing their overall grain boundary energy, as indicated by the roundness of the grain boundary surfaces. This also suggests an overall reduction in the free energy of the

FIGURE 28. Optical Micrograph of a Copper Metal Anode Surface Directly Exposed to Cryolite During Polarization. Stratification of the oxidation layer is apparent, and small dendrites of CuAl_2O_4 can be seen on the surface of the oxidation layer.

system through a more favorable surface-to-volume ratio for each grain. This process may be thermally activated by the temperature of the electrolysis process.

An anode fabricated from the reaction-sintered $\text{NiO-NiFe}_2\text{O}_4\text{-Cu-Ni-X}$ cermet material was polarized for 6 h at 950°C . After completion of the experiment, the cell was disassembled and autopsied. Micrographs of the anode are shown in Figures 33 and 34. The anode showed little wear, and the reaction layer on the surface is only $4\text{ }\mu\text{m}$ thick. Internal porosity increases are minimal, but would be difficult to detect due to the nature of the reaction-sintered cermet microstructure. This anode showed the least amount of wear of all the anodes tested during FY86, and thus, this material warrants further investigation.

No dc polarization sweeps were performed on this cermet. During the polarization experiments, a nichrome lead wire was used rather than platinum, as it was suspected that the materials contained in the cermet would react with

FIGURE 29. Optical Micrograph of a PNL-Prepared $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ Cermet Anode That Was Galvanostatically Polarized for 8 h. Cracking of the anode probably occurred after completion of the experiment.

the platinum lead wire, causing failure. However, the nichrome wire also corroded during the test, causing the cell voltage to change with time. As the cell was being operated galvanostatically, the anode current density remained unchanged. However, it was felt that dc polarization sweeps would be meaningless because the overall cell voltage would contain a small but unmeasurable error due to the corrosion of the nichrome lead wire.

An electrolysis cell was assembled using a $\text{NiO-NiFe}_2\text{O}_4\text{-Cu-Ni}$ anode (21.5-wt% copper, 3.5-wt% nickel). The cell was operated for 7 h at 960°C . Cyclic dc polarization sweeps performed on the anode indicated that the cermet passivated and that no corrosion currents could be detected. The voltammogram obtained for this anode is shown in Figure 35. Micrographs of this anode are

FIGURE 30. High-Magnification Optical Micrograph of the PNL-Prepared NiO-NiFe₂O₄-Cu Cermet Anode Shown in Figure 29. The reaction layer is approximately 30 μm thick. Increase in porosity is apparent.

FIGURE 31. Low-Magnification SEM Micrograph of the PNL-Prepared NiO-NiFe₂O₄-Cu Cermet Anode Shown in Figures 29 and 30. This view shows the surface area of the anode exposed to cryolite during polarization.

FIGURE 32. High Magnification SEM Micrograph of the PNL-Prepared NiO-NiFe₂O₄-Cu Cermet Anode Shown in Figures 29 and 30. This view illustrates the increase in porosity which may be due to an annealing process occurring in the sample during electrolysis.

shown in Figures 36 and 37. This anode is severely corroded, which would seem to contradict the dc polarization results. The severe corrosion is most likely due to alumina starvation of the cell, which may have resulted from an incorrectly batched electrolyte.

Several of the powder metallurgically prepared metal anodes were also tested under dc polarization conditions. None of the metal anodes performed well in the cryolite-based electrolytes. An anode composed of 45-wt% nickel, 30-wt% iron, 10-wt% copper, and 15-wt% chromium was polarized for 6 h at 960°C. After 3 h of galvanostatic operation, the anode was subjected to a cyclic dc polarization sweep. The resulting voltammogram is shown in Figure 38. An oxidation peak was identified at 2.09 V, but the species represented by this peak remain unidentified. Little hysteresis was observed between the forward and reverse trace.

FIGURE 33. Optical Micrograph of a $\text{NiO-NiFe}_2\text{O}_4\text{-Cu-Ni-X}$ Reaction Sintered Cermet Anode After 6 h of Galvanostatic Polarization of 1 A/cm^2 Anode Current Density

The microstructure of the anode is shown in Figures 39, 40, and 41. The anode was covered by a reaction product layer averaging $50 \mu\text{m}$ in thickness. The edge of the anode exhibited more corrosion due to the increase in current density and surface energy at the edge. The reaction product layer is adherent in some areas (Figure 41), and appears as a nonadherent layer in other areas

FIGURE 34. High Magnification Optical Micrograph of the Reaction-Sintered NiO-NiFe₂O₄-Cu-Ni-X Anode Shown in Figure 33. This view shows the surface which has been exposed to cryolite during electrolysis.

(Figure 40). This particular anode was the best performer of the five metal anodes tested during FY86 in that it showed the least amount of visible corrosion when the cell was autopsied.

Other metal anodes suffered from extreme corrosion and oxidation. Several of the compositions were incompatible with the platinum lead wire used to make electrical connections between the potentiostat and the anode. This was because the anode compositions contained aluminum metal which alloyed with the platinum, resulting in brittle failure of the lead wire. From these preliminary results, it was felt that the metal anodes would not be good candidate materials for use as inert anodes. The voltammograms obtained from these materials indicated that a large portion of the current was being used to actively corrode the metal. The metal anodes did not passivate, which would have resulted in excessive aluminum metal pad contamination in commercial Hall-Heroult aluminum reduction cells.

FIGURE 35. Voltammogram of a PNL-Prepared $\text{NiO-NiFe}_2\text{O}_4\text{-Cu-Ni}$ Cermet Anode

FUTURE DIRECTIONS

Most of the candidate anode material screening experiments were completed in FY86. Research in FY87 will focus on the development of the four types of $\text{NiO-NiFe}_2\text{O}_4$ -based cermets studied. These were chosen for further testing based on their microstructures, electrical conductivities, and performance in electrolysis testing. Testing will focus on 30-h wear rate tests of materials in 5- to 15-A electrolysis cells. Full electrical conductivity measurements from

FIGURE 36. Macro View of a PNL-Prepared $\text{NiO-NiFe}_2\text{O}_4\text{-Cu-Ni}$ Cermet
Anode Polarized for 7 h at 1 A/cm^2

FIGURE 37. Optical Micrograph of the Reaction Layer Found on the $\text{NiO-NiFe}_2\text{O}_4\text{-Cu-Ni}$ Anode Shown in Figure 36

room temperature to 950°C will be performed on candidate materials to accurately determine the types of electrical conduction present.

Additionally, experiments will be performed to determine the effect of cathode surface area on the wear rate of the anode. The possibility exists that if the electrolyte becomes saturated with anode constituents, and the rate at which anode impurities plate out at the cathode is mass transport controlled, then the rate of wear may be decreased by decreasing the cathode surface area. Another effort during FY87 will be to develop a viable means of attaching these cermets to connection rods for use in larger cells. At the end of FY87, a candidate material for scaleup to larger Hall-Heroult cells (1000+ A) should be identified, complete with a method of attaching the material to other materials for electrical contact and support.

FIGURE 38. Voltammogram of a Powder Metallurgically Prepared Metal Anode. This anode was composed of 45-wt% Nickel, 30-wt% Iron, 10-wt% Copper, and 15-wt% Chromium.

FIGURE 39. Optical Micrograph of a Powder Metallurgically Prepared Metal Anode Polarized 6 h

FIGURE 40. PNL-Prepared Metal Alloy Anode Showing the Nonadherent Portions of the Product Reaction Layer

FIGURE 41. PNL-Prepared Metal Alloy Anode Showing an Adherent Portion of the Product Reaction Layer

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MATERIALS EVALUATION

C. F. Windisch

SUMMARY

The FY86 objectives for this subtask were to use electrochemical and spectroscopic methods to help develop new inert anodes for the aluminum industry and to determine and broaden the operating range of these anodes. Toward these ends, the electrochemical reactions of the $\text{NiO-NiFe}_2\text{O}_4\text{-Ni}$ and $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermet-anodes^(a) and pure copper metal anodes with molten cryolite were investigated. The anodes were tested under electrolysis conditions using potentiodynamic polarization, cyclic voltammetry, in situ laser Raman spectroscopy, ac impedance methods, and a variety of post-test analytical techniques.

The cermet anodes were chosen because some of their properties were previously investigated by Alcoa Laboratories. Copper metal was studied because it was felt that an understanding of its reaction mechanisms would increase our knowledge of the copper-containing cermet material.

The principal technical accomplishments during FY86 included the following:

- the design, construction, and evaluation of two bench-scale electrochemical cells
- the determination of nickel corrosion in the $\text{NiO-NiFe}_2\text{O}_4\text{-Ni}$ cermet anode material during electrolysis in molten cryolite
- the characterization of copper oxide transformations in $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermet anodes and copper metal anodes
- the collection of ac impedance data on the $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermet in molten cryolite

(a) The cermet anodes were fabricated using $\text{NiO-NiFe}_2\text{O}_4$ powder provided by Alcoa Laboratories. Anodes containing copper metal were prepared by adding 17%-wt% copper metal to the oxide powder. See the Materials Fabrication section of this report for additional details.

- the design, construction, and evaluation of a successful in situ laser Raman spectroscopy cell for studying reactions at anodes in molten cryolite
- the collection of quality spectra of molten cryolite over a range of bath compositions
- the collection of in situ laser Raman spectra of molten cryolite near the $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermet anode during electrolysis.

In general, electrochemical and spectroscopic methods for determining electrochemical reactions were found to give the best results or show the most potential when applied to all-metal electrodes. For this reason, future studies on the electrochemical reaction mechanisms of candidate inert anodes in molten cryolite will focus on metals whose composition is similar to that of the metal phases in the most promising cermet materials.

TECHNICAL PROGRESS

Detailed discussions of the technical progress achieved in FY86 in the investigation of inert cermet anodes are presented below.

Development of Electrochemical Cells

The objective of this work was to develop a standard bench-scale cell for performing short-term ac and dc polarization studies on inert anode candidate materials in molten cryolite. The completion of this work was the first designated milestone for Subtask 3 of the Inert Electrode Program.

Two designs for electrochemical cells (shown in Figure 42) were developed and successfully evaluated in short-term experiments. Both cells employed the inert anode as a small cylindrical specimen partially sheathed in alumina, an $\text{Al/Al}_2\text{O}_3$ reference electrode, and a cryolite bath saturated with alumina. The difference between the two cells was in the design of the cathode. One employed a bare solid metal cathode; the other used an aluminum pad similar to the Hall-Heroult configuration.

Each candidate cell design was investigated using a NiFe_2O_4 -based ceramic anode. The electronic equipment used in these experiments (the PAR Model 368

FIGURE 42. Two Successful Electrochemical Cells Employing (a) a Solid Metal Cathode and (b) an Aluminum Pad Cathode. [Cell components: (A) inert anode, (B) reference electrode, (C) solid metal cathode, (D) aluminum pad, (E) solid metal lead to aluminum pad, (F) TiB_2 substrate, (G) platinum control anode, (H) thermocouple, (I) gas purge tube, (J) alumina crucible, (K) alumina sheathing, (L) cryolite.]

ac impedance system) is outlined in Figure 43. For the inert anode in each cell, dc polarization curves were obtained. In some cases, ac impedance data were also collected. The quality of the polarization data, the reproducibility of these data, and the integrity of the cell during operation were the principal criteria used in the evaluation.

The initial cell design investigated was based on preliminary experiments done in this laboratory and similar experiments performed by Alcoa Laboratories (Weyand et al. 1986). Alcoa used a three-electrode configuration: the inert

FIGURE 43. PAR Model 368 ac Impedance System

anode, a molybdenum cathode, and an $\text{Al}/\text{Al}_2\text{O}_3$ reference electrode. This electrode configuration and variations of it were evaluated in our work. The cell vessel was made of alumina. The electrolyte was formulated from natural Greenland cryolite and AlF_3 to give a bath ratio equal to 1.1. The bath also contained 4% CaF_2 and was saturated in alumina to minimize dissolution of the cell container and alumina-sheathed cell components. Experiments were conducted at temperatures between 960 and 1040°C.

Components of Electrochemical Cells

The following components of the electrochemical cell were investigated and modified as indicated.

Inert Anode. The principal inert anode material used in this preliminary cell development work was the $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermet. (A better "control" anode

may be warranted as described in the next section.) The most favorable arrangement was to sheath the electrode in alumina (at least partially) and to submerge it no more than 1 mm in the molten cryolite.

The inert electrodes were cylindrical specimens about 1.6 cm in length with a terminal area of 0.16 to 0.17 cm². Each specimen was sheathed in an alumina tube whose inner diameter was sized to make a slip fit between the specimen and the tube. As shown in Figure 44, two sheathing configurations were used.

In the design shown in Figure 44a, only the terminal area of the specimen was left unsheathed for exposure to the molten bath. However, scanning electron microscopy/energy dispersive x-ray spectroscopy (SEM/EDS) analysis of cross-sectioned specimens of this design, which had been immersed in the molten bath for up to 6 h, showed significant penetration of electrolyte into the

FIGURE 44. Anode Configurations Employing (a) Alumina Sheathing to the End of the Anode and (b) Alumina Sheathing Retracted from the End of the Anode

narrow gap between the electrode and the alumina tube. Though the penetration occurred, the anode and the alumina tube showed few signs of deterioration. Penetration of the electrolyte into the gap between the anode and the sheathing material may, however, introduce significant uncertainty (about 20% for a 0.25-mm penetration depth) to the specimen's exposed surface area measurement and, in turn, to the current density measurements. To circumvent this problem an alternate anode design was used.

The alternate anode design shown in Figure 44b involved retracting the alumina sheath a significant distance away from the end of the anode material. The anode was then submerged to a depth of 1 to 2 mm in the molten cryolite. While the total exposed anode surface area was unknown during the experiment, it could be determined afterwards by examining the electrode. The advantage of this design was that it prevented the capillary action which had caused the cryolite penetration in the previous design. The principal limitation was that the exposed surface area was known exactly only at the end of the experiment.

Since the cell did not allow for visual monitoring of the electrodes, the extent to which the anode assembly was submerged in the molten cryolite was estimated indirectly using alumina rods. The rods were dipped into the molten bath to gauge its depth and the value was referenced against the length of the electrode body. This approach was found to be successful. Another procedure to detect submersion of the anode, by measuring electrical resistance between the anode and a second electrode, was also evaluated. It was thought that a sudden decrease in resistance as the electrodes were lowered into the electrolyte would indicate the anode had contacted the molten salt. Unfortunately, false readings (indicating the probes were inserted when they were not) were repeatedly obtained with this method. Apparently, cryolite vapors condensed on the electrodes, providing an electrode-to-electrode conductive "bridge" before the probes touched the melt. For this reason, the electrical approach to determining electrode submersion was abandoned in favor of the mechanical method.

In all cases, the electrical lead to the anode was platinum wire. It was channeled through the alumina sheathing tube to make contact with the anode

specimen at a point significantly above the level of the cryolite bath. This design successfully minimized the possibility of an electrical short caused by electrolyte contact with the lead wire.

Control Anode. Recent polarization studies performed at PNL on cermet compositions have shown that these materials may corrode under some conditions. For this reason, it was considered desirable to have available in each experiment a more "inert" material as a benchmark or control for comparing the polarization behavior of new potential anodes. A control electrode is useful in differentiating the effects of bath composition, cell geometry, etc., from properties of the test anode itself. Platinum was evaluated for this purpose and found to be acceptable.

In a typical electrochemical evaluation, a polarization profile for the platinum anode was obtained shortly before or after the inert anode was profiled. Both the platinum anode and the inert anode were tested in the same cell and under the same conditions. Results for the platinum electrode were used to help interpret non-ideal effects observed for the test specimen.

Cathode. The principal difficulties in the design of a suitable electrochemical cell were the development of an adequate cathode material and configuration. Despite being able to obtain reliable polarization data for the anode, the original molybdenum cathode used by Alcoa physically deteriorated in molten cryolite during polarization. This failure was deemed important at the time and numerous other cathode materials and configurations were evaluated. Unfortunately, most of these also exhibited poor durability. Various modes of cathode failures are possible and these are discussed below. The principal assessment is that, in short-term tests, some cathode deterioration can occur without affecting the polarization properties of the anode.

The original cathode design by Alcoa, a coiled molybdenum wire, was successfully used in our laboratory to obtain polarization data on the cermet anodes. However, this cathode showed signs of mechanical failure after only 2 h of testing. To reduce the extent of deterioration, molybdenum was employed as a cathode in various other configurations. These included molybdenum wire of different diameters, molybdenum wire protected and completely enclosed in an alumina sheath, and a molybdenum plug sheathed in alumina with one large flat

area exposed to the electrolyte medium. In most cases, polarization data were successfully collected. However, post-test analysis of cathode samples revealed significant interaction of molybdenum with molten cryolite 2 h after contact. Complete encasement of the molybdenum cathode in alumina was unsuccessful since it disrupted ion transport, causing the potentiostat to overload. SEM/EDS analyses of the molybdenum cathodes showed significant corrosion when the cathodes were exposed to cryolite for 40 min. X-ray diffraction analysis indicated that one of the principal corrosion products was MoO_2 .

Other solid metal electrode materials were also investigated as potential cathodes. These included tantalum, platinum, and tungsten. The materials were tested sequentially in the same electrochemical cell using the electrode assembly shown in Figure 45. The assembly contained a large-diameter alumina tube through which the different cathodes could be inserted. Each material was tested in cryolite for about 40 min. Polarization data were successfully collected using all of the cathode materials; however, post-test analyses showed that significant cryolite/cathode interaction occurred in most cases and that the extent of this reaction was different for each metal. Tantalum corrosion was similar to molybdenum as revealed by microscopic analysis. The platinum cathode also corroded, and results of SEM/EDS analysis suggested the mechanism involved platinum alloying with the aluminum metal that formed at the cathode during electrolysis. Tungsten gave the best performance of all of the solid metal cathodes tested in the 40-min tests. SEM/EDS analysis showed very little corrosion for tungsten and no corrosion products could be detected by x-ray diffraction. More recent studies, however, show that for electrolysis over longer time intervals, 2 to 3 h, significant corrosion of tungsten can occur. This corrosion may involve reaction with oxygen generated at the anode, which would be found in larger quantities in longer-term tests.

Graphite was also evaluated as an alternative cathode material. However, it too reacted, particularly at the vapor phase interface above the cryolite melt near the point of contact between the platinum and the graphite cathode. Oxygen gas is believed to have caused the reaction. Because of the debilitating effects of oxygen on graphite at these temperatures, it is recommended

FIGURE 45. Configuration for Testing Solid Metal Cathodes. The large alumina tube facilitated the exchange and repositioning of cathodes during a single experiment.

that, unless better control of vapor composition is achieved (by using a more efficiently purged system), graphite should not be used as the cathode material.

Other cathode designs investigated in this work were based on the Hall-Heroult molten aluminum cathode. In design (a) shown in Figure 46, molten aluminum was placed in the bottom of the electrochemical cell and allowed to wet a TiB_2 substrate that had been attached to the bottom of the alumina crucible using Sauereisen Electrotemp Cement No. 8 (Sauereisen Cement Co., Pittsburgh, Pennsylvania). Electrical contact with the aluminum was made

FIGURE 46. Molten Aluminum Cathodes Using (a) an Aluminum Pad Configuration and (b) a Probe-Type Arrangement

through a metal lead. The lead was partially sheathed in alumina to protect it from the molten cryolite. Molybdenum and tungsten were evaluated as electrical lead materials. Both corroded over a 2-h period with molybdenum showing the most severe attack. Tungsten was more successful but still showed a "thinning" effect, probably due to its limited solubility in molten aluminum.

A variation of the Hall-Heroult cathode, employing the molten aluminum cathode in a probe-type arrangement as shown in Figure 46(b), was also

investigated. The utility of the probe design is that it could be reused, unlike the aluminum "pad" which would have to be prepared anew for each cell. Unfortunately, this design failed, apparently due to plugging of the conduction hole which was required for charge transport across the electrode body boundary.

In summary, of all the cathode materials and configurations tested, two designs were found to give the best results. These are shown in Figure 42. The first design employs a solid metal cathode, preferably tungsten. This cathode is recommended for its ease of assembly and because a minimum of dissolved aluminum is required. The second design uses an aluminum pad for experiments where a closer simulation of the Hall-Heroult cell is necessary.

Reference Electrode. The reference electrode used in this work was developed by J. W. Burgman (Burgman, Leistra, and Sides 1986) and is shown in Figure 47. This electrode was found to function adequately and was the only reference design employed. It remained in good condition and was reusable after 4 h of contact with molten cryolite saturated with alumina.

Electrolyte Composition. Excess alumina powder was added to the cryolite bath to protect the various alumina-sheathed cell components from gradual dissolution. The amount of alumina added in each case was twice the weight required for saturation.

Post-test optical analysis of the frozen bath showed a fairly uniform electrolyte matrix of cryolite and alumina. The alumina did not appear to "settle out." Post-test inspection showed very little dissolution of the various alumina cell components over a 6 h test period.

Temperature Control. Initial studies suffered from problems associated with the furnace and its controller. The potentiostat was found to be sensitive to current/voltage fluctuations in the external devices. Electromagnetic interference (EMI) generated by the furnace resulted in widely varying current and voltage readings at the potentiostat which caused the unit to overload. Various attempts were made to eliminate this problem including the use of different furnaces and controllers and the incorporation of EMI shields around the

FIGURE 47. Reference Electrode Based on the Design by Burgman, Leistra, and Sides (1986)

electrode assemblies. The problems were later corrected by using an isolation transformer to eliminate high-level transients in the line cord. In addition, a furnace with non-inductively wound elements was purchased to correct potential problems from continuous ac signal pickup.

In the earlier studies, the temperature was allowed to climb to about 1040°C and then, to prevent EMI, the furnace was shut off. Data were collected

with the furnace off for a period of 10 min or until the temperature had fallen to about 970°C. With the design improvements, studies were conducted under isothermal conditions.

Pre-electrolysis. Pre-electrolysis of molten cryolite is sometimes performed to remove electroactive bath impurities. No pre-electrolysis was performed in this work, initially because of problems associated with the furnace. The potentiostat was unable to control current/voltage as long as the furnace was on. However, experiments conducted with the newer furnace (in the absence of EMI problems) indicated pre-electrolysis was not necessary. Polarization data collected using a platinum anode shortly after its immersion in freshly prepared molten cryolite showed no residual currents below the theoretical decomposition potential for alumina. This suggests that no significant amounts of impurities, which would give rise to these currents, were present.

Experiment Duration. In the cell development work, experiment duration varied widely depending on the number of variables examined in a given run. For more typical anode evaluations, the steps and their approximate durations are shown in Table 3. The optional ac impedance studies include experiments performed at dc potentials differing from the open circuit potential. In addition, other types of polarization experiments may be conducted including dc polarization as a function of time or environmental factors.

TABLE 3. Experiment Duration

Step	Duration, h
Thermal equilibration/melting	1.5
Electrode insertion/submersion tests	0.2
Pre-electrolysis (may not be required)	0 to 3.0
ac impedance study on control anode (optional)	0.5
dc polarization study on control anode	0.5
ac impedance study on test specimen	0.5
dc polarization study test specimen	0.5
Optional ac impedance studies	0 to 1.0
TOTAL	3.7 to 7.7

Atmosphere Control. Precautions were taken to minimize variations in vapor phase composition. In particular, the molten salt bath was continuously blanketed with argon gas to reduce the levels of water vapor and facilitate the removal of oxygen, generated during electrolysis, above the liquid. Purging with argon gas was used merely to maintain a steady-state atmospheric composition.

Cell Container. Alumina was used as the cell container material for all of the experiments in this work. In a typical experiment, a 100-mL crucible was employed. All of the electrodes and secondary probes were sheathed in alumina. To minimize dissolution of the crucible and sheathed components, the molten cryolite bath was saturated in alumina.

An interesting phenomenon observed in this work was the appearance of cryolite on the outside of the alumina container after a test was terminated. SEM/EDS analysis was performed on a cross section of an alumina crucible that had contained molten cryolite to determine whether the container was at all permeable to the bath. No significant amounts of cryolite-related chemical species were detected in the alumina container walls, suggesting the mode of transport of cryolite was surface diffusion and/or evaporation and condensation. To minimize problems associated with "moving" cryolite, the alumina crucible walls should be reasonably high or a second high-walled container should be used.

Conclusions. Two successful designs for short-term electrochemical polarization studies on inert anodes were developed (see Figure 42). They differ only in their cathode configurations. The solid metal (preferably tungsten) cathode should be used for rapid short-term tests when the presence of significant amounts of aluminum metal is undesirable or unnecessary. The aluminum cathode should be used when conditions closer to an operating Hall-Heroult cell are required.

Nickel Corrosion in the $\text{NiO-NiFe}_2\text{O}_4$ -Ni Cermet Anode

Potentiodynamic polarization data were obtained on anodes fabricated from the $\text{NiO-NiFe}_2\text{O}_4$ all-oxide mix provided by Alcoa. The all-oxide composition was used because it would, presumably, not corrode and therefore would serve as a

good referee material with which to compare corrosion-susceptible anodes. One of the polarization curves for this material is shown in Figure 48 (Curve a). Relatively high current densities were obtained at potentials below the decomposition potential for alumina, suggesting the participation of electrolytic reactions other than the decomposition of alumina. It is possible that electroactive bath impurities were present and that these were participating in the overall oxidation process at the anode. However, as discussed below, polarization data collected using a platinum "control" anode (Curve b) indicated that the phenomenon was caused by the anode material itself and not the electrolyte.

Even without pre-electrolysis, bath impurities had no significant impact on the polarization curves in this work. In our experiments, a pure platinum anode was employed in the same cell as the ceramic anode under investigation. Prior and subsequent to obtaining electrochemical data on the ceramic material, polarization curves were obtained for the platinum electrode. As shown in Figure 48 (Curve a), residual currents were observed for the material at potentials significantly below the theoretical decomposition potential, 2.2 V, while for the platinum anode (Curve b) these currents were not observed. This same difference in behavior was observed repeatedly over the course of a 6-h experiment during which the ceramic electrode was polarized (alternating with the platinum anode) to varying extents. If these residual currents were due to bath impurities, they would have been observed for both the ceramic and platinum anodes. The fact that they were not suggests the currents arose from processes involving the inert anode material itself.

Discovery of Metallic Phase

Optical microscopy and SEM/EDS data suggested the residual currents were due to a metallic phase whose presence was unexpected. These analyses revealed three separate phases, and x-ray diffraction indicated that one of these phases was metallic nickel. The presence of a metallic phase suggests the possibility of corrosion processes similar to those reported by Alcoa for the $\text{NiO-NiFe}_2\text{O}_4\text{-Ni}$, the Alcoa 6846 or nickel-containing cermet that gave rise to corrosion currents below the oxygen evolution potential (Weyand et al. 1986).

Based on discussions with consultant Warren Haupin, the metallic nickel phase probably arose from the electrochemical reduction of NiO during anode

FIGURE 48. The dc Polarization Curves for (a) the NiO-NiFe₂O₄ Anode and (b) a Platinum Anode. (Obtained shortly after immersion in alumina-saturated molten cryolite at 980°C. Scan rate was 10 mV/s.)

fabrication. NiO may have been reduced by an organic binder during the sintering process. New anode preparation procedures were subsequently developed which led to more reliable anode compositions. These procedures are reported in the Materials Fabrication section.

Copper Transformations in the NiO-NiFe₂O₄-Cu Cermet and Copper Metal Anodes

Alcoa Laboratories found that the NiO-NiFe₂O₄-Cu cermet material performed well as an anode in molten cryolite in Hall-Heroult cells (Weyand et al. 1986). To understand the reactions occurring at the NiO-NiFe₂O₄-Cu anode during electrolysis, potentiodynamic studies were performed on the cermet and also on copper metal anodes. In these studies, current-versus-potential data were obtained that provided information on the chemical transformations of copper occurring during electrode polarization.

Potentiodynamic Studies on the NiO-NiFe₂O₄-Cu Cermet Anode

Polarization curves were obtained for the NiO-NiFe₂O₄-Cu material in molten cryolite saturated with alumina at 980°C. As shown in Figure 49 (Curves a and b), significant residual currents were observed below the theoretical decomposition potential when the specimen was polarized immediately after immersion. Above the decomposition potential, the polarization curve showed high cell resistance (small i-V slope) and large hysteresis effects. These phenomena were not observed for a platinum electrode under the same conditions (Curve c). This suggests the residual currents and resistance behavior were a result of processes germane to the cermet material and not due to electrolysis of bath impurities. As shown in Figure 50, polarization of the NiO-NiFe₂O₄-Cu material under galvanostatic conditions for about 3 h at 1 A/cm² reduced the magnitude of these non-ideal effects (particularly the hysteresis). This suggests some amount of pre-electrolysis using the inert anode may be required to "condition" it prior to obtaining a reproducible polarization curve.

Although electrolysis at 1 A/cm² for 3 h reduced most of the hysteresis effects observed in the potentiodynamic data, residual currents at potentials below the decomposition potential for alumina were present. These currents became the subject of additional studies. As shown in Figure 50, a small "peak" was observed at 2.16 V in the forward oxidation trace in the polarization curve for the NiO-NiFe₂O₄-Cu material. Since this peak may arise from the oxidation of copper in the metallic phase of the cermet, studies were performed on copper metal anodes in molten cryolite in an effort to better understand this reaction.

FIGURE 49. The dc Polarization Curves for the NiO-NiFe₂O₄-Cu Anode in the (a) Forward and (b) Reverse Directions, and (c) for a Platinum Anode. (Obtained shortly after immersion in alumina-saturated molten cryolite at 980°C. Scan rate was 10 mV/s.)

FIGURE 50. Cyclic Voltammogram for the NiO-NiFe₂O₄-Cu Cermet in Alumina-Saturated Molten Cryolite at 960°C. (Obtained after polarization at 1 A/cm² for 3 h. Scan rate was 10 mV/s. This voltammogram was obtained in the Materials Development subtask of the Inert Electrode Program.)

Potentiodynamic Studies on Copper Metal Anodes

As shown in Figure 51, cyclic voltammograms (polarization curves showing both forward and reverse potential scans) for copper metal in molten cryolite saturated with alumina gave one resolved oxidation wave and two reduction waves below 2.30 V. The single oxidation peak occurred at about 2.18 V. The reduction waves occurred at 1.96 V and 2.00 V. As shown in Figure 52, polarization of copper metal to different switching potentials revealed additional information, including a second oxidation wave at 2.44 V. In addition, the intensities and potentials of the reduction waves were also found to depend on the scan rate.

FIGURE 51. Cyclic Voltammogram for Copper Metal in Alumina-Saturated Molten Cryolite at 980°C. [The forward trace (a) shows oxidation processes; the reverse trace (b) shows reduction processes. Scan rate was 10 mV/s in the forward direction and 20 mV/s in the reverse direction.]

FIGURE 52. Cyclic Voltammograms for Copper Metal Alumina-Saturated Molten Cryolite at 980°C. Shows effect of switching potential: (a) 2.14 V, (b) 2.18 V, (c) 2.24 V, (d) 2.28 V, (e) 2.50 V. Scan rate was 10 mV/s in the forward direction and 20 mV/s in the reverse direction.

The principal oxidation wave in Figure 51 may be explained by considering the standard electrochemical potentials for the most probable copper oxide reactions at 980°C. The standard emf for the reaction

is -2.187 V (National Bureau of Standards 1971). The negative of this value (the potential required to cause the reaction to proceed as written) is close to the observed potential for the principal oxidation wave for copper in molten cryolite saturated with alumina. This suggests the primary anode reaction under these conditions is the oxidation of Cu_2O to CuO .^(a) The reduction wave at 2.00 V is assigned to the reverse of Reaction (1).

The above assignment is consistent with the morphology of deposits observed on the copper metal electrodes after polarization. The deposits were composed mainly of Cu_2O and CuO , as determined by x-ray diffraction, x-ray photoelectron spectroscopy, and Auger spectroscopy. Cu_2O was the major component and appeared as a red layer adjacent to the copper substrate. The layer included a minor amount of a black phase, presumably CuO . No significant copper fluoride or aluminum species were detected, suggesting the principal electrochemical transformations involved copper oxides.

A copper aluminate phase was also identified in the deposits formed in all of the experiments on copper metal. X-ray diffraction analysis indicated the compound was CuAlO_2 . It was previously suggested that the copper aluminate was responsible for copper passivation in molten cryolite (Weyand et al. 1986). In our work, however, SEM/EDS analysis suggested that the copper aluminate always formed on the outside surface of the copper oxide and not adjacent to the metal.^(b) This suggests that the copper aluminate was a product of reactions

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- (a) The direct oxidation of Cu_2O to CuO according to the reaction $3\text{Cu}_2\text{O}(\text{s}) + \text{Al}_2\text{O}_3(\text{s}) = 6\text{CuO}(\text{s}) + 2\text{Al}(\text{l})$ is also probable, having a standard emf at 980°C equal to -2.141 V.
- (b) SEM/EDS analyses revealed the presence of copper and aluminum in this single phase which is assumed to be copper aluminate based on XRD analyses.

between Cu_2O and alumina and/or cryolite. It is more likely that the copper oxides which are formed near the copper surface are passivating.

Other evidence also suggests Cu_2O is the "starting point" for oxidation when a copper electrode is externally polarized in molten cryolite saturated with alumina. Specifically, Cu_2O formed or was stable on copper metal under these conditions even in the absence of an applied electric field. A copper metal specimen submerged in the same molten salt bath as the copper electrode whose data were described above gave significant albeit not as much corrosion as the electrolyzed material. A red Cu_2O deposit was also observed on the unpolarized specimen. Unlike the electrode sample, however, not as much black CuO deposit was observed.

These results corroborate the voltammetry data suggesting that a direct reaction occurs between copper metal and alumina in molten cryolite at 980°C under open circuit conditions. This reaction results in a generally passive Cu_2O layer which remains stable below 2.18 V. Above this potential it converts to CuO according to Reaction (1).

The oxidation peak at 2.44 V has not been assigned to a specific reaction at this time. It may involve the formation of a soluble copper species, perhaps containing copper in the $3+$ oxidation state (Whiting, Mamantov, and Young 1973). The potential is high enough to suggest this, although no thermodynamic data on trivalent copper species could be found to support the assignment. Some copper dissolution was observed in these experiments, as evidenced by the discovery of significant amounts of copper metal at the cathode in post-test analysis.

Cyclic voltammograms on copper metal in molten cryolite with alumina at concentrations below saturation were also obtained. These data were collected in experiments using a molten salt bath prepared from a mix containing no added alumina. During these experiments, alumina concentrations increased due to dissolution of the cell's alumina components but, presumably, for most of the short-term studies the alumina remained at concentrations below saturation. These data indicate that a number of important changes occur for copper metal in melts containing low concentrations of alumina which were not observed for alumina-saturated melts.

To explain these results, it was proposed that Cu_2O formation is an important reaction of copper in molten cryolite. At high alumina concentrations, Cu_2O forms or is stabilized under open circuit conditions and only its oxidation to CuO is observed in the cyclic voltammograms. In contrast, at low alumina concentrations, Cu_2O formation is incomplete under open circuit conditions. Under these conditions, the formation of Cu_2O from copper is observed as a distinct oxidation wave.

Due to the similarity between the cyclic voltammograms of copper metal and the $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermet, it is likely that Cu_2O and CuO and their transformations are important in the reported passivation of the metal phase of the cermet. Future research should shed more light on the roles these oxides play at higher current densities and potentials and over longer time intervals.

The ac Impedance of $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ Cermet

Measurements of ac impedance have been used to study a variety of electrochemical phenomena. In these studies, a very small (5- to 10-mV peak-to-peak) ac potential is applied to the electrode of interest and the resulting ac current is measured. The resulting electrical impedance is calculated as a function of frequency of the applied potential. By comparing these data to the behavior expected for a standard electronic circuit (assuming a suitable circuit can be found), the electrode capacitance and charge transfer kinetics of important electrochemical processes can be determined. The ac impedance techniques offer the advantage of providing minimal perturbation of the test system, thus reducing errors caused by the measuring technique itself. In addition, ac impedance methods can be used to determine the uncompensated resistance of the electrochemical cell.

The PAR Model 368 ac impedance measuring system used in this work is shown in Figure 43. Data collection and processing were carried out by an Apple IIe microcomputer using the PAR Model 368 ac impedance software.

Nyquist Plot for the $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ Cermet

The Nyquist plot (Z' versus $-Z''$ plotted as a function of frequency, where Z' and Z'' are the real and imaginary part of the complex impedance) obtained in the vicinity of the open circuit potential is shown in Figure 53 for the

FIGURE 53. Nyquist Plot for the NiO-NiFe₂O₄-Cu Cermet in Alumina-Saturated Molten Cryolite at 980°C. Data were obtained about the open circuit potential 1.86 V. Frequency range was 0.5 Hz to 10 kHz.

NiO-NiFe₂O₄-Cu cermet material. This plot has the appearance of a partial semicircle at higher frequencies and a linear relationship at lower frequencies, a behavior which is characteristic of a charge transfer process that becomes mass transfer-limited at low frequencies. It can be modeled by the electronic circuit also shown in Figure 53. Fitting a semicircle to the higher frequency portion of the curve gives a charge transfer resistance (R_{ct}) equal to 3 ohms·cm² and a double layer capacitance (C_{dl}) equal to 884 μF. The uncompensated resistance (R_u) was about 1 ohm·cm². The phase angle of the low frequency portion of the curve is 21°, which is about one-half of the theoretical value (45°) obtained for an electronic circuit containing a Warburg impedance (Z_w) to simulate mass transfer effects (Bard and Faulkner 1980).

According to DeLevie (1967), an electrode with semi-infinite pores gives a phase angle one-half of that for an equivalent planar electrode, while the absolute magnitude of the porous electrode impedance is proportional to the square root of the planar electrode impedance. This predicts a phase angle of 22.5° for a porous electrode under diffusion control, which is very close to the phase angle observed for the $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ cermet electrode at low frequencies. This suggests that the porosity of the cermet electrode is important for reactions occurring under open circuit conditions.

In Situ Laser Raman Spectroscopy

Electrochemical methods have proven to be helpful in characterizing reactions at anodes during electrolysis, particularly in determining under what potential and current density conditions these reactions occur. Nevertheless these methods suffer from one principal limitation: they provide very little information regarding the identity of molecular species undergoing transformations during electrochemical polarization. Spectroscopic techniques, on the other hand, can provide this information if they can be adapted to in situ analysis. In this work, in situ laser Raman spectroscopy has been applied to the reactions occurring at candidate inert anode materials during electrical polarization in molten cryolite.

In laser Raman spectroscopy, the sample of interest is irradiated with a laser beam and the inelastically scattered light is collected and analyzed. The inelastically scattered light, whose frequency components are plotted as a function of intensity in a Raman spectrum, contains information about the molecules in the sample and can be used as a fingerprint for specific molecular species. Furthermore, it can be used to identify chemical changes caused by perturbation of the sample; for example, electrical polarization.

Backscattering Raman Spectroscopy Cell Configuration

In order to adapt this technique to studying reactions at the interface of an anode during electrolysis in molten cryolite, a number of important spectroscopy cell design criteria must be met. These criteria include the following: 1) the cell material must remain fairly resistant to corrosion in molten cryolite; 2) the cell wall material must remain transparent to the laser

beam during the course of the experiment; 3) the laser beam must interrogate a portion of the reacting medium which is representative of chemical changes occurring at the anode interface; 4) the temperature of the cell must be measurable and controlled; and 5) the apparatus should allow for maximum flexibility of anode positioning so that the instrument can be easily "peaked up" on Raman signals due to the chemical species of interest.

Since the material of primary interest was the $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ anode, the first Raman spectroscopy cell designed used the backscattering configuration shown in Figure 54. In this design a laser beam entered the cell from below, through an optical quality quartz window, and was scattered when it hit the flat anode specimen. The scattered light was collected by a flat mirror and directed into the Raman spectrometer for analysis.

Raman spectra were generated using a Spex Model 1403 Raman spectrometer and two different detection systems. The first system used a photomultiplier tube and a Spex Datamate controller for data reduction and analysis. The second used a Tracor Northern TN-6133 diode array detector and a TN-1710A multichannel analyzer. The former detection system gave better resolution ($\pm 1 \text{ cm}^{-1}$) but required much more time to collect spectra (about 20 min/spectrum), while the latter setup had the advantage of faster data collection (about 30 s/spectrum) but poorer resolution ($\pm 4 \text{ cm}^{-1}$). Since the spectroscopic cells used in this work degraded optically with time during the experiment (limiting the duration of the experiment to about 2 h), it was important to collect the Raman data as quickly as possible. For this reason the diode array detector became the system of choice, particularly in the latter stages of the experimental work. Other important experimental conditions for the Raman experiments included the use of the 488.0-nm line of a Spectra Physics Ar^+ laser for excitation and the employment of slit widths of 400 cm^{-1} . A Solarton Model 1186 electrochemical interface was used for control of the anode current.

Raman Spectrum of $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$

Using the backscattering configuration, Raman spectra of the $\text{NiO-NiFe}_2\text{O}_4\text{-copper}$ anode in molten cryolite at 970°C contained in quartz spectroscopic cells showed no detectable bands that could be assigned to either the anode

FIGURE 54. In Situ Laser Raman Spectroscopy Cell Employing Backscattering Geometry. The cell material was quartz and the bottom window was of optical quality. The electrode assembly consisted of a working electrode made of the anode test material, a tungsten cathode, and a thermocouple.

material or cryolite. The spectra were dominated by features attributed to the quartz container. No spectral changes were observed during electrolysis at 970°C.

The Raman signals for NiO-NiFe₂O₄-Cu were not observed because of the intrinsically weak nature of these bands. To demonstrate this, Raman spectra were obtained for the anode material in air at room temperature, outside of the spectroscopic cell. The spectrum shown in Figure 55 was one of those obtained and is typical for a metal oxide spinel structure (White and DeAngelis 1967). It showed several very weak bands in the 450 to 725-cm⁻¹ region. The most prominent band occurred at 686 cm⁻¹ and is probably due to a relatively isolated symmetric stretching vibration of the metal (probably Fe⁺³)-oxygen octahedra. The very weak nature of these bands (even under ideal conditions) suggests that chemical changes involving NiFe₂O₄ will be very difficult to detect under in situ conditions.

FIGURE 55. Raman Spectrum of NiO-NiFe₂O₄-Cu Taken in Air at 25°C Using Backscattering Configuration

Molten cryolite has been shown by other researchers to exhibit several Raman bands although these were observed under very different sampling conditions (Gilbert, Mamantov, and Begun 1975). Since the probability of observing changes in the $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$ material was low due to the weak nature of its Raman scattering intensities, it seemed appropriate to focus efforts on chemical changes in the molten cryolite near the anode interface during electrolysis. Electrolysis reactions, corrosion reactions, and other interactions of the anode and the electrolyte involving soluble species should be discernible using this approach, provided, of course, that the species of interest were Raman active. In order to use this approach, however, a better Raman spectroscopic cell design was required. This new cell would have to permit a more thorough interrogation of the cryolite melt near the anode interface and would remove the effects of quartz which previously interfered with spectral analysis.

Forward Scattering Raman Spectroscopy Cell Configuration

The improved Raman spectroscopy cell configuration using a forward laser scattering geometry developed in this work is shown in Figure 56. Sapphire cells (3-in. long, 0.5-in. OD tubes of optical quality, purchased from Saphikon of Milford, New Hampshire) were used in place of the quartz cells to remove the interference from vibrational features due to the cell material. Since these cells are manufactured with plugs made of non-optical material, a backscattering configuration was unsuitable. A forward scattering geometry was used instead, which provided the added bonuses of better power throughput of the scattered light to the Raman spectrometer and easier adjustment of the anode during an experiment. The furnace designed and built for these forward scattering experiments is also shown in Figure 56. It consisted of a heated quartz tube with three orthogonally positioned windows. The center window functioned as an observation port.

The electrode assembly used in the in situ laser Raman spectroscopy studies consisted of the following: 1) the candidate inert anode sheathed in alumina with about 0.3 cm^2 of surface area exposed to the molten cryolite, 2) a cathode made of tungsten wire partially sheathed in alumina with its lower section exposed and coiled about 1 cm below the anode, and 3) a platinum

FIGURE 56. In Situ Laser Raman Spectroscopy Cell Employing Forward Scattering Geometry. The cell material was sapphire. The electrode assembly consisted of a working electrode made of the anode test material, a tungsten cathode, and a thermocouple.

thermocouple. In an in situ laser Raman experiment, about 4 g of alumina-saturated cryolite with a bath ratio of 1.1 were added to the sapphire cell and heated to 980°C. Using the observation port, it was visually ascertained that the bath was molten. The electrode assembly was then lowered into the melt. After the electrodes were submerged, the laser beam was adjusted using a lens to bring the focal point of the beam directly below the anode interface. The anode position was also adjusted to optimize scattering conditions. Raman spectra of the molten cryolite were collected with no current applied to the cell and then with current applied. All the while, the cell was monitored visually to make certain that it was operating without any problems.

Raman Spectra of Molten Cryolite

As shown in Figure 57 (Curve a), the Raman spectrum of alumina-saturated molten cryolite taken in the absence of applied current at 980°C with a bath

FIGURE 57. Raman Spectra of Molten Cryolite at 980°C Containing (a) 12% Alumina and (b) 0% Alumina. (Spectra were obtained using the forward scattering configuration.)

ratio of 1.1 exhibited principal Raman bands at about 548 cm^{-1} and 618 cm^{-1} . These bands were assigned to Al-F octahedral and tetrahedral vibrations, respectively. Spectra of molten cryolite containing no added alumina were also obtained; one of these is shown in Figure 57 (Curve b). The spectra of the alumina-saturated and alumina-free samples were very similar. Subtraction of one of these spectra from the other failed to reveal any significant differences between them. (Minor variations were attributed to different background intensities.) This was surprising since bands attributed to Al-O-F moieties were expected for the alumina-containing melt. Gilbert, Mamantov, and Begun (1975) identified bands below 600 cm^{-1} arising from Al-O-Al vibrations. These bands were very weak (especially for high bath ratios like those studied in this work), but they could be resolved using spectral subtraction routines. It is likely that Gilbert, Mamantov, and Begun were more successful because they

used a "more sensitive" windowless spectroscopic cell which has been shown to give high-quality spectra for molten cryolite although it cannot be readily adapted to electrolysis experiments.

In Situ Laser Raman Spectra of Molten Cryolite
Using NiO-NiFe₂O₄-Cu Anode

In situ laser Raman spectroscopy was performed during the electrolysis of molten cryolite at 980°C. The cryolite was formulated with a bath ratio of 1.1 and saturated with alumina. A forward scattering laser geometry was employed with the laser beam positioned as close as practical to the NiO-NiFe₂O₄-Cu anode. Spectra were obtained at various time intervals during electrochemical polarization at both 0.1 and 1.0 A/cm².

As shown in Figure 58, Raman spectra obtained in this study contained the two principal bands for molten cryolite which were observed in previous experiments. These bands occurred at 524 and 618 cm⁻¹ in this study. The 524 cm⁻¹ vibration exhibited a somewhat lower frequency than observed previously (i.e., 548 cm⁻¹). This was attributed to a number of factors. First, a different detection and signal analysis system was used in the two studies. In addition, different amounts of radiation backgrounds were observed for the two studies which, although subtracted from the experimental data, may have been partially unremoved, giving small frequency shifts. In addition to the two principal Raman bands, a third band at 396 cm⁻¹ was observed, which is also consistent with previous Raman spectra of molten cryolite.

As shown in Figure 58, no significant change in the Raman spectrum of the molten cryolite near the ceramic anode occurred at a current density of 1 A/cm². The Al-F octahedral and tetrahedral species do not appear to be affected by the electrolysis process. The same may not be the case for the Al-O-F moieties; however, their spectral features (very weak bands obscured by the Al-F vibrations) were not observed in this study. No new spectral features were observed during electrolysis, suggesting that minimal deterioration of the ceramic anode occurred (assuming that the potential corrosion products are Raman active).

FIGURE 58. Raman Spectra of Alumina-Saturated Molten Cryolite Near the NiO-NiFe₂O₄-Cu Cermet Anode During the Passage of (a) 0 Current and (b) 1 A/cm². Spectra were obtained using the forward scattering configuration.

Future in situ laser Raman studies will focus on all-metal anodes to determine whether corrosion processes can be observed using this technique, and to simulate the reaction chemistry occurring near the metallic phase of the cermet electrode materials.

FUTURE DIRECTIONS

Research performed in FY86 with both electrochemical and spectroscopic techniques suggests that the most promising systems for studying corrosion mechanisms are those using pure metal anodes. Cyclic voltammetry was successfully applied to copper metal in the determination of important oxidation and

reduction processes during electrode polarization. In situ laser Raman spectroscopy, although unsuccessful in applications involving cermet materials, may prove more useful in studies on corrosion of pure metals. Future work, therefore, will primarily involve corrosion studies on pure metal anodes whose compositions will mimic those of the metal phases of the cermets. These studies should help determine which compositions are the most corrosion resistant and under what operating conditions corrosion resistance and anode lifetimes are optimized.

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reduction processes during electrode polarization. In situ laser Raman spectroscopy, although unsuccessful in applications involving certain materials, may prove more useful in studies on corrosion of pure metals. Future work, therefore, will primarily involve corrosion studies on pure metal anodes whose compositions will mimic those of the metal phases of the ceramics. These studies should help determine which compositions are the most corrosion resistant and under what operating conditions corrosion resistance and anode lifetimes are optimized.

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LABORATORY CELL TESTS

B. J. Wrona

The objectives of this subtask are to support the development of inert anodes for use in Hall-Heroult cells by the aluminum industry and to optimize the operating parameters of these cells such as bath temperature, alumina content, bath composition, and bath ratio.

SUMMARY

Two laboratory-scale Hall-Heroult cell test systems have been designed and constructed for testing inert anodes. The design and construction of the test systems allows for versatility in testing parameters. They were initially used for 20-h tests of 3.2-cm-diameter anodes. Only minor modifications are needed for conducting 60-A tests on 7.5-cm-diameter anodes. The test systems are currently being used to conduct 20-A Hall-Heroult cell experiments.

Baseline aluminum reduction cell tests have been performed on 3.2-cm-diameter anodes at 965°C for 20 and 30 hours. The tests have successfully demonstrated that an anode dissolution rate of less than 2.54 cm/yr is feasible with low amounts of impurities in the aluminum produced. These test results are encouraging for the development of inert anode materials.

TECHNICAL PROGRESS

Corrosion of inert anodes during operation of Hall-Heroult cells presents a major concern in the development of inert anodes because it reduces the useful life of the anode and adds impurities to the aluminum. Copper cermet anode life can be significantly increased if the cell is operated using optimized bath chemistry, cell temperature, and operating parameters. However, for inert anodes, this combination of optimum conditions needs to be determined and verified with reproducible results.

To determine optimum operating conditions for an aluminum reduction cell several orderly series of tests will be conducted. An initial series of experiments was conducted to provide baseline cell and copper cermet anode

performance information. The purpose of the baseline tests was twofold: 1) to define test system performance characteristics, and 2) to quantify anode wear and degradation on an incremental basis as a function of time. The baseline tests were conducted on 3.2-cm-diameter copper cermet anodes for time periods of 20 and 30 hours. The baseline tests have been completed and the results are reported in a section that follows.

The plan calls for a second series of tests to be conducted to screen a broad range of cell operating parameters. Information from the first series of baseline tests will serve as a basis to compare with the results of the second series of screening tests. Output from the second series of tests will be used to identify parameters critical to cell efficiency and anode material longevity. A test matrix has been developed to determine the relative importance of operating parameters such as bath composition, bath ratio, alumina content, bath temperature, anode current density, and cathode current density.

Experimental Procedures

Laboratory cell experiments were conducted using the cell design shown by the schematic drawing in Figure 59. This cell, which is shown in the photograph in Figure 60, has some features that simulate a large-scale aluminum reduction cell. These features include cryolite electrolytic bath, the anode and cathode electrodes, an aluminum pad, and production of aluminum by the electrolytic process. An Inconel 600 can provided the containment for the test cell. The bottom inner surface of a graphite crucible served as the cathode and an Inconel 600 rod threaded into the upper surface of the crucible provided the electrical connection. An aluminum pad (2.54 cm high) was inserted into the cell prior to the start of the test to mitigate floating of the aluminum metal produced during electrolytic operation of the cell. Because of a similar density, molten aluminum has a tendency to float in the liquid bath, causing electrical shorting between the anode and cathode and degradation of the anode.

Crucible side walls were electrically isolated from the anode by two alumina sleeves inserted adjacent to the crucible wall. The primary purpose of the alumina liners was to reduce degradation of the anode due to electrical shorting of the anode with the side walls of the crucible. In addition, the liners simulated the insulating side walls of a conventional Hall-Heroult

FIGURE 59. Schematic Drawing of a Laboratory Aluminum Reduction Cell

cell. Graphite paste was used to join the alumina liners to the bottom surface of the graphite crucible in an attempt to seal the molten bath into the inner alumina liner. Coarse alumina powder was poured into the annulus between the sleeves to act as a baffle to molten bath flow and as a reserve of alumina to reduce the dissolution rate of the outer alumina liner, in case of penetration of the inner sleeve.

Alumina powder was fed to the cell through a two-pieced alumina tube. A narrow tube was needed above the cell because a lack of space precluded the use of a larger diameter tube. However, the end of the tube inserted into the cell had to be wider, because bath vapors condensing in the lower portion of the

FIGURE 60. Photograph of 20-A Laboratory Cell

tube could block the flow of alumina powder. To accommodate these conditions, an alumina tube was fabricated from two different-diameter alumina tubes bonded together with an alumina-based Saureisen paste. In an additional attempt to prevent blockage of the feed tube, an argon purge gas was passed through the feed tube to sweep out bath vapor condensation.

Current was supplied to the cell and controlled with a Trygon System 50-A dc power supply. Temperature was monitored with type K thermocouples. The vertical position of the anode was monitored with a linear variable differential transformer (LVDT). Data was recorded with an IBM personal computer interfaced with a Fluke Helios A/D converter. A furnace, used to heat the cell, was started at night with a preset timer, for significant time savings.

Alumina refractories were purchased from Coors Porcelain Company. Graphite crucibles were machined in-house from existing materials. Inert anodes were of the 5324-17 wt% copper cermet composition described in the

Materials Development section of this report. The brazed alloy electrical connection to the anode is also described under Materials Development.

Electrical current was controlled manually with the power supply to a setting of 1 A/cm^2 based on the entire immersed area of the anode. The vertical position of the anode was controlled and adjusted with a converted camera tripod. The alumina concentration was maintained at saturation during the test, assuming a 100% current efficiency.

Four samples of electrolyte (for bath ratio determination) were removed from the cell at predetermined intervals during the cell test. The samples were removed from the molten bath by ladling the liquid into a long quartz sampling tube which had a small slot cut about 3 cm above the bottom of the tube.

Anode dimensions were measured before and after the test to determine dimensional changes. Anodes were cut in half using a diamond-edged cut-off saw blade. The anode halves were polished metallographically, and examined microscopically to determine the extent of copper depletion and degradation of the anodes.

Aluminum metal was retrieved after cooldown of the cell to determine the overall current efficiency. The aluminum metal samples were submitted to be chemically analyzed for anode constituents such as iron, copper, and nickel.

Results and Discussion

The purpose of the initial Hall-Heroult cell experiments was to provide baseline data for subsequent screening tests to determine critical cell operating parameters. In addition, anode corrosion, as measured by the copper depletion rate at the anode surface and the purity of the aluminum metal produced, provided information for evaluating screening test results.

Figure 61 shows an aluminum pad before and after a 20-h Hall-Heroult cell test to demonstrate the quantity of aluminum produced during the test. Whether the molten aluminum pad assumed different configurations during cell operation is not known.

FIGURE 61. Aluminum Pad Before Test (on left) and After Test (on right)

Figure 62 shows the typical surface appearance of anodes before and after testing. The 3.2-cm-diameter copper cermet anode was tested for 20 h at 965°C,

FIGURE 62. Anodes Before and After 20-h Test

with an average current density of approximately 1 A/cm^2 , and a bath ratio of 1.07. There is a thin coating of bath material on the anode tested for 20 h, but no evidence of degradation. Figure 63 shows a cross-sectional view of the tested anode at a higher magnification, demonstrating that the test had little effect on the microstructure of the anode. Figure 64 is a photograph showing the lower portion of the same anode at an even higher magnification. Again, there are no signs of anode deterioration.

The localized areas of the anode marked A, B, C, and D are shown at higher magnifications in Figure 65. Figure 65A shows the bottom middle surface of the anode; it can be seen that the depletion zone of the copper is less than 0.05 mm. Figure 65B shows the lower corner of the anode with very little deterioration on the bottom surface, but a slightly wider region of corrosion on the vertical surface (side) of the anode. The dark region of the anode surface is a thin layer of bath material that has penetrated and solidified on

FIGURE 63. Low-Magnification Cross Section of Copper Cermet Anode After a 20-h Test

FIGURE 64. Higher Magnification of Lower Portion of Copper Cermet Anode Tested for 20 h

the vertical surface. Figure 65C shows the vertical side surface at a higher elevation. Surface degradation is minimal and copper depletion is estimated at approximately 0.06 mm, which extrapolates into a depletion zone of less than 2.5 cm/yr. Figure 65D shows the interior region of the anode and demonstrates the uniform distribution of copper and copper particle size.

These encouraging anode performance results were confirmed by the anode test conducted for 30 h. The anode microstructures and dissolution rates of the 30-h test are typical of those observed for the 20-h test. The current efficiency for the 30-h test was approximately 85%. Current efficiency was determined by dividing the weight of aluminum produced by the theoretical quantity of aluminum that could be produced during the test, assuming 100% efficiency of the electrolytic process.

Chemical analyses were performed to determine the percentage of anode constituents in the aluminum after the tests. Percentages of anode constituents in the aluminum following the tests are listed in Table 4. After accounting for the aluminum pad inserted before the test, the percentages of copper, iron,

FIGURE 65. Higher Magnification of Regions A, B, C, and D of the Anode Shown in Figure 64. The anode regions shown are (A) Bottom Center, (B) Bottom Corner, (C) Vertical Side, and (D) Interior.

TABLE 4. Anode Constituent Impurities in Aluminum Following Tests

	<u>20-h Test, %^(a)</u>	<u>30-h Test, %^(b)</u>
Copper	0.13	0.18
Iron	0.16	0.39
Nickel	<u>0.135</u>	<u>0.27</u>
Totals	0.425	0.84

(a) Values are not adjusted because aluminum was lost during post-test sectioning in order to examine cell.

(b) Values are adjusted to account for aluminum pad inserted before start of test.

and nickel in the 30-h test are slightly higher than targeted values. According to aluminum industry representatives, low percentages of copper and iron are not a problem because they are desirable constituents that may be added to commercial alloys. Nickel impurities are an issue of concern however, primarily because the industry has no information on the effects of low percentages of nickel in aluminum.

It is anticipated that anode wear and corrosion will be significantly reduced when the cell is operated using optimized bath chemistry, cell temperature, and operating parameters. This combination of optimum conditions will be determined in future laboratory cell studies.

The present acceptance criteria for assessing the performance of anodes tested in the laboratory cells are as follows:

- anode dissolution rate of less than 2.5 cm/yr
- aluminum purity greater than 99.5% based on inert anode constituents
- good integrity of the anode electrical connection.

In tests conducted to date, the copper cermet anodes have met the dissolution rate acceptance criteria, and the prospects are good for meeting the aluminum purity criteria with future developmental work. Based on these encouraging results, the probability is high that the copper cermet anode materials being tested and developed in this program will be acceptable for use in commercial aluminum reduction cells. Therefore, the schedule should be

substantially accelerated for 1) ongoing development of the electrode materials, 2) concurrent scaleup to larger electrodes and test cells, and 3) transfer of technology to industry. Acceleration of the schedule is necessary and critical to be responsive to the needs of industry in the United States.

FUTURE DIRECTIONS

Following the recently initiated series of screening tests, a third series of tests will be performed to focus on critical cell operating parameters. This test series will serve to fine-tune critical cell operating parameters identified in the second test series, to maximize electrode life while maintaining high cell efficiency.

A fourth series of experiments will be conducted concurrently to verify the performance of titanium diboride-bearing cathodes, cathode paste materials, and 3.2-cm-diameter copper cermet anodes. Details of these tests are discussed in the cathode development section of this report. All of the previously described tests will be conducted using 20-A cells.

The plan calls for a subsequent series of tests to be conducted in 60-A cells with electrodes scaled up in size to 7.5-cm diameters. The purpose of these tests is to verify that the previously fine-tuned critical parameters remain optimized despite the change in anode geometry with the increase in electrode diameter.

Following confirmation of the acceptability of inert anodes in the 60-A cells, the results will be extended to 1000- to 3000-A cells and finally to cells of 20,000 A and larger. The ultimate result will be the demonstration of durable anodes with substantial energy and electrode fabrication cost savings.

This experimental effort, the technical approach, and test matrices draw heavily from work performed for a DOE program by Alcoa in pioneering the development of inert anodes.

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A fourth series of experiments will be conducted concurrently to verify the performance of titanium dioxide-bearing cathodes, cathode paste materials, and 3.2-cm-diameter copper current anodes. Details of these tests are discussed in the cathode development section of this report. All of the previously described tests will be conducted using 50-A cells.

The plan calls for a subsequent series of tests to be conducted in 50-A cells with electrodes scaled up in size to 7.6-cm diameter. The purpose of these tests is to verify that the previously fine-tuned critical parameters remain optimized despite the change in anode geometry with the increase in electrode diameter.

Following completion of the acceptability of inert anodes in the 50-A cells, the results will be extended to 1000- to 3000-A cells and finally to cells of 50,000 A and larger. The ultimate result will be the demonstration of durable anodes with substantial energy and electrode fabrication cost savings.

This experimental effort, the technical approach, and test matrices drawn heavily from work performed for a DOE program by Alcoa in pioneering the development of inert anodes.

LARGE-SCALE TESTS

B. J. Wrona

This subtask has both technical and business objectives. Technical objectives include 1) demonstration of the technical viability of large-scale electrodes, and 2) identification and resolution of everyday cell operating problems prior to commercialization. Business objectives include 1) demonstration of the economic viability of large electrodes, and 2) transfer of the technology to the aluminum industry.

SUMMARY

The primary purpose of this subtask was to develop a plan for the future demonstration of the technical viability of large inert anodes in a large-scale aluminum reduction cell. The encouraging results of the 1-1/4-in.-diameter anodes tested in 20-A laboratory cell experiments provided positive support for the decision to proceed with larger-scale tests. The recommended approach is to confirm the results of the 20-A cell studies with tests in 60-A cells, followed by tests at 1000 to 2500 A, and finally in industry-scale cells of 20,000 A or more. This would permit verification and prooftesting of a number of bath chemistries, cell operating parameters, anode fabrication methods and specifications, anode handling and transfer, and numerous other daily cell operating considerations. The large anodes required would be fabricated by a commercial ceramic manufacturing company using technology developed at PNL. The selection of two anode fabrication vendors is advised to promote competitive pricing and delivery.

TECHNICAL PROGRESS

A preliminary plan has been formulated to address the issues of Hall-Heroult cell scaleup, emphasizing a cooperative effort between PNL and the aluminum industry. PNL will design, construct, and operate an intermediate-sized cell on site, to facilitate ongoing development and improvement of electrode materials. This will permit PNL to identify and resolve daily problems

associated with operation of a large cell. The direct participation of industry will be encouraged. Specifically, electrode retrofit of an existing 5000-A test cell, at either Alcoa, Kaiser, or Reynolds Metals, will be pursued.

A wide range of considerations is involved in the design, construction, and operation of an intermediate-sized cell at PNL. Following is a preliminary list of the room requirements, test cell requirements, electrode acceptance criteria, etc., necessary for operation of an intermediate-sized, 1000- to 2500-A, test cell operation at PNL.

Room Requirements

- floor space of 70 m² (7 m x 10 m)
- overhead crane (2-ton capacity)
- electrical utilities (1000- to 2500-A capability)
- offgas capability (hood, filters, pump, controls)
- offgas cleanup
- tentative location selected (Materials Research Center)
- storage space for 2000-kg alumina
- storage space for 2000-kg aluminum
- easy access to large door.

Test Cell Requirements

- self-heating test cell (2500-A maximum)
- 16 anodes (approx. 16-cm diameter)
- 4 anode assemblies (4 anodes per assembly)
- cost estimate of cell including electrical system (\$100,000)
- durable sidewall materials (SiC)
- 2-cm wall thickness, steel construction
- design prototype with scaleup in mind
- anode adjustment mechanism
- monitoring of anode connection integrity
- continuous anode voltage/current measurements by computer
- alumina feed system
- siphoning molten aluminum
- provisions for transfer, handling and storage of large aluminum ingots.

Anode Acceptance Criteria

- anode dissolution rate less than 2.54 cm/yr
- high integrity connections
- metal purity greater than 99.5%, based on anode constituents
- anode fabrication cost/life economic analysis better than that of carbon anodes
- energy savings compared to current anode materials.

Cathode Acceptance Criteria

- metal purity greater than 99.5%, based on cathode constituents
- cathode dissolution rate less than 2.54 cm/yr
- cost/life economic analysis better than carbon cathodes.

Anode Preheat/Cooldown Furnace

- temperature capability of 1100°C
- working capacity of 8 anodes
- overhead hoist capability.

Environmental and Safety Requirements

- environmental impact statement to be written, reviewed, and approved
- safety document to be written, reviewed, and approved.

Subtasks and Schedule

- development of technical approach for PNL and existing commercial cell)
- conceptual design of cell facility
- identification of components for procurement:
 - electrical
 - mechanical
 - anodes
 - cathodes
 - sidewalls
 - anode connections
 - cell containment

- molds
- alumina
- flux
- cost estimate for PNL large cell
- cost estimates for industrial cells
- decision on location of PNL cell
- decision on PNL and existing industrial cell
- detailed design of PNL cell
- environmental impact statement prepared
- safety document prepared
- procurement of materials
- construction of PNL cell
- operation of PNL cell
- materials characterization and evaluation
- economic assessment
- technology Transfer.

Tests at 60 A are being conducted to confirm the results of the initial 20-A cell tests with inert anodes. After the 60-A tests, the subtasks listed above should be pursued as funding becomes available. The 5000-A-capacity industrial test cell will be a separate phase of the program that will start (budget permitting) when the 1000- to 2500-A cell demonstrates technical viability.

CATHODE MATERIALS EVALUATION

K. H. Pool

SUMMARY

The purpose of this study was to measure the initial wear rates of TiB_2 carbon-containing cathode materials ($\text{TiB}_2\text{-G}$) under electrolytic conditions. Parameters evaluated included bath ratio, current density, and aluminum pad thickness.

Two types of $\text{TiB}_2\text{-G}$ materials were supplied by the Great Lakes Carbon Company for evaluation. The materials differed in the concentration, size, and ways the separate TiB_2 and carbon phases were interconnected. The addition of graphite to TiB_2 permits the use of smaller amounts of lower cost TiB_2 in the cathodes, improves the thermal shock resistance of the cathode, and results in lower cost fabrication routes and the ability to fabricate more complex cathode shapes.

A cell and a sampling technique were developed to monitor Al_4C_3 build-up during transference cell operation. In order to measure initial wear rates, the tests were limited to 8 h. Based on Al_4C_3 accumulation rates observed in the 8-h tests, extrapolated annual wear rates of $\text{TiB}_2\text{-G}$ under thin aluminum film conditions can be calculated. Linear extrapolation yields annual wear rates of 4.6 to 26 cm/yr. Parabolic extrapolation yields values of 0.18- to 0.67-cm wear in the first year's service. (Both extrapolations assume 50 vol% carbon in $\text{TiB}_2\text{-G}$.)

Micrographs of post-test $\text{TiB}_2\text{-G}$ specimens suggest that during short-term tests, TiB_2 particles are loosened from the $\text{TiB}_2\text{-G}$ matrix and are removed from the active electrolysis surface as a slurry of suspended TiB_2 particles in liquid aluminum. In only one test was evidence of Al_4C_3 found in the $\text{TiB}_2\text{-G}$ cathode reaction interface layer or in the frozen thin film of Al metal adhering to the cathode at the end of the test. Since only limited evidence for Al_4C_3 could be found in the $\text{TiB}_2\text{-G}$ cathode reaction interface layer, the Al_4C_3 formed must be rapidly transported to the cryolite bath for dissolution and dispersion rather than persist as Al_4C_3 dissolved in aluminum metal.

TECHNICAL PROGRESS

The objective of the work discussed in this report was to determine the wear rate and wear mechanism of $\text{TiB}_2\text{-G}$ as a replacement for carbon as the cathode material in a Hall-Heroult aluminum reduction cell. $\text{TiB}_2\text{-G}$ is relatively inert to chemical attack by Hall-Heroult electrolyte (cryolite) and is wetted by molten aluminum, whereas carbon and graphite are not. Compared with carbon-based cathodes, swelling and erosion can be greatly reduced by using $\text{TiB}_2\text{-G}$. Wetting of $\text{TiB}_2\text{-G}$ by aluminum and a sufficiently low $\text{TiB}_2\text{-G}$ wear rate may lead to the use of dimensionally stable drained cathodes in Hall-Heroult cells. Consequently, the anode/cathode distance of an operating cell could be reduced and more consistently controlled.

Cell Design

The design of the transference cell shown in Figure 66 evolved from a series of preliminary designs. The cell design that was evolved excluded oxygen penetration to prevent oxidation of the formed Al_4C_3 , and allowed electrolysis times up to 10 h. The cryolitic-alumina bath was contained in a closed aluminum oxide cell.

Two types of $\text{TiB}_2\text{-G}$ were supplied by Great Lakes Carbon Corporation--Type A and Type B--for testing. A "standard cryolite bath" (bath ratio = 1.07 by weight, saturated with Al_2O_3 and containing 5% CaF_2) was used in limiting slope configurations--horizontal and vertical. Both materials were also tested in a cryolite bath with a ratio of 2.0 and were mounted in the vertical configuration. These latter tests were included to examine the possibility that high bath ratios, in which the equilibrium solubility of Al_4C_3 is much reduced, would lead to lower wear rates. Temperatures were $980^\circ \pm 15^\circ\text{C}$ for standard cryolite bath tests and $990^\circ \pm 10^\circ\text{C}$ for bath ratio = 2.0 tests. The Al_4C_3 concentration in the bath samples was measured by reacting the samples with water to produce methane and then measuring the amount of methane produced in a gas chromatograph.

Materials Examined

Micrographs of the $\text{TiB}_2\text{-G}$ materials supplied by Great Lakes Carbon are shown in Figure 67. The graphite phase, which is black in the micrographs,

FIGURE 66. Laboratory-Scale Transference Cell

appears to be more continuous in the Type A material than in the Type B material. Porosity is also dark in the micrographs. The TiB_2 phase in the Type B material appears more continuous than in the Type A material. The large TiB_2 particles, which appear to be agglomerates of finer particles, are finer in the Type A material than in the Type B material. The agglomerates appear more uniform in size in the Type A material than in the Type B material. The relative concentrations of the graphite, the TiB_2 , the porosity, and the degree of graphitization in the materials were not measured.

a) Type A

b) Type B

FIGURE 67. Microstructure of $\text{TiB}_2\text{-G}$ in the As-Received Condition

Transference Cell Results

Tests were conducted to determine the effect of material type, current density, bath ratio, sample position (either vertical or horizontal) on wear rate. Results are summarized in Table 5. Rates are reported in terms of the amount of carbon lost from the surface of the sample ($\text{mg C/cm}^2\text{-h}$) and carbon thickness lost per year (cm/yr). For the latter calculation, it was assumed that the $\text{TiB}_2\text{-G}$ was 50 vol% TiB_2 and that the carbon was lost uniformly from the surface. Lower volume fractions of carbon would proportionately increase the calculated wear rate.

Both Type A and Type B $\text{TiB}_2\text{-G}$ exhibited higher wear rates when tested in the horizontal configuration than when tested in the vertical configuration. There is some evidence from post-test photomicrographs that electrolysis was not completely confined to the exposed horizontal surface. If this was the case, then the true current density was less than that given in Table 5 and corresponding wear rates are less than those tabulated.

The results of a typical successful test (EB-17) are summarized in Figure 68. If a linear model is assumed, the slope of the fitted straight line ($0.054 \text{ g Al}_4\text{C}_3/\text{h}$) can be used to calculate wear rate by the following equation:

$$\frac{0.054 \text{ g Al}_4\text{C}_3}{\text{h}} \times \frac{36 \text{ g C}}{144 \text{ g Al}_4\text{C}_3} \times \frac{1}{13.9 \text{ cm}^2} \times \frac{10^3 \text{ mg}}{\text{g}} = 0.97 \text{ mg C/cm}^2\text{-h}$$

Extrapolating this wear rate to one year, the following annual wear rate is predicted:

$$\frac{0.97 \text{ mg C}}{\text{cm}^2\text{-h}} \times \frac{24 \text{ h}}{\text{day}} \times \frac{365 \text{ day}}{\text{yr}} \times \frac{10^{-3} \text{ g}}{\text{mg}} = 8.54 \text{ g C/cm}^2\text{-yr}$$

Using the density of graphite = 2.25 g/cm^3 , a linear wear rate of 3.80 cm C/yr can be calculated. Finally, if the $\text{TiB}_2\text{-G}$ specimen is 50 vol% carbon, the wear rate of the $\text{TiB}_2\text{-G}$ surface is 7.6 cm/yr . If the $\text{TiB}_2\text{-G}$ specimen is 25 vol% carbon rather than 50 vol%, the $\text{TiB}_2\text{-G}$ wear rate is 15.2 cm/yr . For comparison purposes throughout this report, 50 vol% carbon is used in all calculations.

TABLE 5. Summary of Results of Successful Transference Cell Tests

Test	Material	Sample Position (a)	Bath Ratio	Area, cm^2	Current Density, A/cm^2	Wear Rate			
						Linear Extrapolation		Parabolic Extrapolation	
						$\text{mg C}/\text{cm}^2\text{-h}$	$\text{cm}/\text{yr}^{(b)}$	$\text{mg C}/\text{cm}^2\text{-h}^{1/2}$	$\text{cm}/\text{yr}^{(b)}$
EB-23	TiB ₂ -G-A	H	1.07	2.3	1.3	2.51	20	7.58	0.63
EB-25	TiB ₂ -G-A	V	1.07	9.8	0.8	1.22-0.89	9.5-7.0	3.53-4.49	0.29-0.37
EB-30	TiB ₂ -G-A	V	2.00	10.0	0.8	0.83	6.5	2.78	0.23
EB-17	TiB ₂ -G-B	V	1.07	13.9	1.04	0.98	7.6	3.31	0.28
EB-24	TiB ₂ -G-B	V	1.07	9.8	0.8	0.65	5.1	2.78-3.10	0.23-0.26
EB-29	TiB ₂ -G-B	H	1.07	2.3	0.87	1.9-0.8	15-6.3	4.17	0.35
EB-27	TiB ₂ -G-B	V	2.00	10.0	1.2	0.54	4.2	1.92	0.156

(a) H = horizontal; V = vertical.

(b) Assumes TiB₂-G is 50 vol% C.

FIGURE 68. Aluminum Carbide Content of Bath as a Function of Electrolysis Time for Test EB-17

These calculations really represent the initial recession rate of carbon only. Whether the entire sample surface would erode at the same rate as the carbon would depend on the integrity of the TiB_2 network remaining as the carbon is removed. If the TiB_2 network does maintain its structural integrity as carbon is removed, Al_4C_3 formation would be at progressively deeper layers away from the original cathode surface. The Al_4C_3 would have to diffuse through a thicker and thicker layer of Al/TiB_2 in order to disperse in the bath. Such a situation would lead to a diffusion limited wear rate and, thus, a parabolic Al_4C_3 accumulation rate would be predicted. That is, a diffusion controlled model predicts that a plot of wt Al_4C_3 in bath versus $\sqrt{\text{time}}$ should be linear. The transference cell data were fitted to this model and results

are included as the last two columns in Table 5. Overall, the statistical "goodness-of-fit" favors neither the linear nor parabolic model. Note that the last column of Table 5 represents the wear calculated for the first year of exposure. Figure 69 depicts behavior observed in several of the successful tests. In these cases, parabolic curve fits were somewhat better than linear fits.

Two tests, EB-27 and EB-30, were done with a cryolitic bath ratio of 2.0 and are the only tests in which the amount of Al_4C_3 found in bath samples exceeded the equilibrium solubility values. The higher-than-saturation values

FIGURE 69. Aluminum Carbide Content of Bath as a Function of Electrolysis Time for EB-25

of Al_4C_3 found in several samples indicate that both truly dissolved and suspended particles of Al_4C_3 were probably included in the samples.

During system testing, a graphite specimen was used as a horizontal cathode in the transference cell. This test provided baseline data for the rate of Al_4C_3 formation at cathodic graphite not under thick aluminum pad conditions. Since molten aluminum does not "wet" graphite, simultaneous exposure of the graphite to liquid aluminum and molten cryolite took place. The calculated wear rate was 78 cm/yr. The Al_4C_3 content of samples taken during the graphite test is graphically displayed in Figure 70 as a function of time up to 5 h. The test was discontinued after 7 h. Al_4C_3 build-up in the bath was linear with time.

The linear wear rate of carbon under thick pad conditions is known to be about two orders of magnitude less than the value quoted above. This high value is attributed to concomitant production of aluminum and sodium at the high current density used in this test (3 A/cm^2). Metallic sodium is known to intercalate and weaken graphitic structures, leading to accelerated wear. It is not known whether the wear rate would have been reduced if the cell had been operated at a more typical value of about 1 A/cm^2 .

Metallographic Analysis

Both types of TiB_2 -G were soak tested in cryolite for 48 h. Optical micrographs of Type B samples revealed evidence of some dissolution of the cathode material in the cryolite bath. Attack by the cryolite was more evident in the SEM micrographs. The formation of a scale on the TiB_2 -G as well as particles within the bath material can be seen in the SEM micrographs.

Elemental analysis showed the presence of particles in the cryolite that were highly enriched in titanium. The morphology of these particles is different from that of the TiB_2 particles in the original TiB_2 -G. There was a lower level of titanium in the scale (reaction product layer between the bath and cathode) compared with the unreacted cathode material. The boron analysis was inconclusive but tended to show low levels in both the scale and the bath. The TiB_2 appears to be dissolving, and a Ti-rich phase is forming in the bath that has a higher titanium concentration than the TiB_2 -G itself.

FIGURE 70. Aluminum Carbide Content of Bath as a Function of Electrolysis Time for Test EB-14

Based on the above analysis, the cryolite penetrated the $\text{TiB}_2\text{-G}$ through the porous network. Concurrently, it was dissolving (reacting with) the TiB_2 to form some complex titanium/cryolite mixture in the scale. Some of the titanium apparently reprecipitated, upon cooling, in the bath near the scale. These precipitates had a different morphology from that of the original TiB_2 and were highly titanium enriched.

Metallographic and SEM Analysis of $\text{TiB}_2\text{-G}$ Tested in a Transference Cell

Figure 71a shows a cross section of the aluminum typically deposited on a horizontal $\text{TiB}_2\text{-G}$ specimen (EB-16). In Figure 71b, the enlargement of Region A in Figure 71a shows that the aluminum is separated from the $\text{TiB}_2\text{-G}$ substrate.

FIGURE 71. a) Cross Section of Type A TiB₂-G Cathode in Test EB-16 b) Enlargement of Region A in Figure 71a

Cryolite was observed clinging to the aluminum. Cryolite had also penetrated into the TiB₂-G. In fact, traces of cryolite were observed near the center of the TiB₂-G specimen. There was no evidence of aluminum carbide at the interface. The needle-like phase in the aluminum contained significant titanium and zirconium. The zirconium could have come from the ceramic cement used in mounting the test specimen. There was only a small amount of this phase in the deposited aluminum.

In the EB-26 test (Figure 72), there appears to be no interaction between the aluminum and the TiB₂ particles. Rather, the aluminum replaced the original carbonaceous matrix. As a result, there was an adherent layer of aluminum on the cathode.

As on the other cathodes tested, the aluminum formed or flowed along the sides of the cathodes. The appearance of the interface at Region B was very similar to that at the bottom surface of the cathode in Figures 73 and 74. The needle-like aluminum oxide particles were also present in the frozen bath near the aluminum layer.

Micrographs of the cathode reaction layer are shown in Figures 75 and 76 after a test at 1 A/cm² for 1-1/2 h. The test was terminated due to failure of

FIGURE 72. Type B Cathode Tested in the Vertical Position in Test EB-26

FIGURE 73. Magnification of Region A
in Figure 72

FIGURE 74. Magnification of Region B
in Figure 72

the cathode lead connection; therefore, test results are not included in Table 5. As in previous examples, there appears to be a multitude of discrete TiB_2 particles suspended in the electrolytically formed aluminum. In Figure 76, one can see what may be an Al_4C_3 phase between the TiB_2 -G and the Al/ TiB_2 surface layer. This is the only evidence for reaction product in these studies.

FIGURE 75. Cross Section of Aluminum Deposited on $\text{TiB}_2\text{-G}$ in Test EB-20. An Al_4C_3 phase may be present at position A.

FIGURE 76. Higher Magnification of Reaction Area Shown in Figure 75. Phase at reaction interface between $\text{TiB}_2\text{-G}$ and Aluminum may be Al_4C_3 .

Figure 16. Higher magnification of reaction area shown in Figure 15. Phase at reaction interface between Ti-6Al-4V and Aluminum may be Al₂O₃.

CATHODE BONDING DEVELOPMENT

C. H. Schilling and N. C. Davis

The objective of the Cathode Bonding Development task is to develop design alternatives for retrofitting commercial Hall-Heroult cells with TiB_2 -based cathode materials.

SUMMARY

The open literature was reviewed to examine the feasibility of reported approaches for retrofitting Hall-Heroult cells with TiB_2 -based cathodes. Based on this review, prime candidate approaches were selected and evaluated for short-duration wear behavior using soak tests and laboratory-scale electrolysis experiments.

- Experiments indicated that coatings of TiB_2 , TiB_2 -graphite, and TiB_2 -AlN may eventually detach from graphite substrates because of chemical erosion of graphite beneath the coatings. Based on the literature review, a drawback to retrofitting cells with this approach is that misalignment of the anode and cathode caused by carbonaceous cell bottom heavage may produce nonuniform electrode current distribution, localized electrode wear, and increased cell energy consumption and operating costs.
- Short-duration electrolysis experiments were performed to evaluate replaceable drained cathode fixtures using a TiB_2 -graphite composite that rests, unattached, on carbonaceous cell bottoms. Results indicated this method is feasible for evaluating larger-scale inert or consumable anode electrolysis without major modification to existing commercial cell bottom designs. Based on the literature review, retrofitting cells with this approach has the drawback of interpolar spacing misalignment caused by cell-bottom chemical erosion and heavage. Retrofitting with this approach may indeed reduce power consumption, although maximum power savings would result from using more dimensionally stable cell bottom materials.

- Replaceable anode-cathode fixtures are attractive retrofit approaches, based on the literature review and discussions with industry experts. Stable alignment of interpolar spacings can be achieved by 1) the use of mechanical spacers attached between anode and cathode surfaces, and 2) the lack of physical contact between the fixtures and cell bottoms. However, material wear rates and wear mechanisms should be experimentally evaluated to determine optimum spacer materials and mechanical configurations for the fixtures and external attachments. In addition, electrolyte recirculation through the interpolar spacing should be tested as a means of replenishing alumina feed and removing gas bubbles.
- Based on the electrolysis experiments and the literature review, prime candidate wear-resistant cathode materials for retrofit applications were determined, including TiB_2 -graphite composites produced by Great Lakes Research Corporation, sintered composites of AlN powder and carbothermically reduced TiB_2 powder, and sintered high-purity TiB_2 powder produced by the Alcoa plasma process. Among these materials, TiB_2 -graphite composites are attractive for retrofit applications because of the ease of fabricating complex shapes.

TECHNICAL PROGRESS

Accomplishments in FY87 included measuring of thermal expansion rates, development of cements, bonding of TiB_2 -AlN materials to graphite, soak testing, testing of a replaceable cathode design, and testing of methods for sintering coatings of TiB_2 and ZrB_2 on graphite, and a review of relevant literature.

Literature Review

An open literature review was performed to evaluate the feasibility of several methods of retrofitting existing commercial cells with TiB_2 -based cathode materials, and the results were used to select prime candidate cell designs for subsequent laboratory experiments. A report entitled "Stable Attachment of TiB_2 -Based Cathodes for the Aluminum Industry: Review and

Recommendation" summarizes applicable patents, alternative coating techniques, and developmental research performed by several aluminum companies.

Based on this review, prime candidate cell designs for laboratory evaluation were determined. These include 1) composite tiles bonded to carbonaceous cell bottoms using a graphite intermediate layer (Kaplan et al. 1982), 2) replaceable drained cathode fixtures that rest, unattached, on carbonaceous cell bottoms (Goodnow and Payne 1982), and 3) replaceable anode/cathode fixtures using inert mechanical spacers to align interpolar spacing (Jarrett and Hornack 1985). Laboratory studies in FY86 examined the first and second design alternatives mentioned above, while FY87 experiments are planned to evaluate replaceable anode-cathode fixture design concepts. The summary report also identified three prime candidate cathode materials for use with all of the above cell designs: 1) TiB_2 -graphite composites produced by Great Lakes Research Corporation, 2) sintered composites of AlN powder and carbothermically reduced TiB_2 powder, and 3) sintered high-purity TiB_2 powder produced by the Alcoa plasma process.

Thermal Expansion Measurements

It is necessary to minimize thermal expansion stresses in TiB_2 -based coatings to maintain adhesion to carbonaceous cell bottom materials. To provide a qualitative measure of compatibility, the thermal expansions of several candidate substrates and coating were measured. Thermal expansion coefficients are shown in Table 6 for polycrystalline TiB_2 , TiB_2 - AlN composites, prebaked carbon cathode block materials, and various grades of graphite. Expansion measurements were performed in an argon atmosphere between 25 and 1050°C; all the data were linear functions of temperature.

As indicated in Table 6, the prebaked carbon cathode block materials have significantly lower thermal expansion coefficients than all of the TiB_2 -based materials evaluated. In contrast to prebaked carbon cathode block, graphite is available with a wide range of thermal expansion coefficients. However, graphite is more costly than prebaked carbon cathode block, and high expansion graphites are more costly than lower expansion grades. Based on these results, it does not appear feasible to directly bond TiB_2 to prebaked carbon cathode block or to low-expansion graphites unless the bonds themselves can accommodate

TABLE 6. Thermal Expansion Data

Materials	Thermal Expansion Coefficient $\times 10^6$, $^{\circ}\text{C}^{-1}$ (25 to 1050 $^{\circ}\text{C}$)
Graphite:	
Union Carbide 1370	5.6
Union Carbide 1857	6.3
Great Lakes H-463	9.0
Great Lakes H-478	9.1
Poco AXF-50	8.9
Poco PPE 109-15	8.9
Prebaked Carbon Cathode Block ^(a)	2.0 to 5.0
Polycrystalline TiB_2	9.1
Polycrystalline $\text{AlN}^{(b)}$	4.8, 5.7
50 vol% TiB_2 - 50 vol% AlN	8.5 to 8.9
33 vol% TiB_2 - 67 vol% AlN	7.6

(a) Manufacturer reported values.

(b) Long and Foster (1959) report 4.8×10^6 , $^{\circ}\text{C}^{-1}$ at 20 to 500 $^{\circ}\text{C}$ and 5.7×10^6 , $^{\circ}\text{C}^{-1}$ at 500 to 1000 $^{\circ}\text{C}$.

thermal expansion stresses caused by heating to cell operating temperatures or during high-temperature processing of the bonds. For example, Townsend and Boxall (1984) showed that thermal stresses upon cooling may cause tensile failure of TiB_2 coatings electrodeposited at high temperatures; these authors illustrated that these TiB_2 coatings remain adherent if their expansion coefficients are close to that of the substrate material.

TiB_2 - AlN materials were investigated because they are reported to have significantly lower thermal expansion coefficients than polycrystalline TiB_2 , thereby allowing bonding to a wide variety of medium-expansion graphites (Long and Foster 1959; Skaar and Croft 1973; Keihn and Keplin 1967; Kaplan et al. 1982; Richards, Berry, and Johnston 1967 and 1968). As indicated in Table 6, several graphites have expansion coefficients that are comparable to TiB_2 - AlN coatings. PNL measurements also demonstrate that an increase in AlN content reduces the thermal expansion coefficient of the TiB_2 - AlN composite. However,

the 50 vol% TiB_2 · 50 vol% AlN composites produced by PNL exhibited thermal expansion coefficients that were much nearer to polycrystalline TiB_2 than expected. In contrast, much lower thermal expansion coefficients (5 to 7×10^6 , $^\circ\text{C}^{-1}$) have been reported for 50 vol% TiB_2 · 50 vol% AlN produced by Kaplan et al. (1982). The high values obtained from the PNL composites may have been attributable to the high degree of connectivity of the TiB_2 phase, as indicated in the polished microstructure appearing in Figure 77.

The above simple comparison of thermal expansion coefficients is intended only to provide a qualitative measure of thermal expansion compatibility. A more rigorous analysis should examine time dependent evolution of multiaxial stresses as a result of specific bond processing scenarios and cell operating conditions. Such an analysis should consider pre-existing internal stresses in the materials to be bonded, size and shape effects controlling thermal expansion stresses, cell bottom heavage caused by sodium intercalation and salt

FIGURE 77. Polished Surface of 50 vol% TiB_2 · 50 vol% AlN Bonded to Union Carbide 1370 Graphite. TiB_2 is the light-colored phase appearing in the coating; the high degree of connectivity of the TiB_2 may have caused the thermal expansion of the coating to resemble that of polycrystalline single phase TiB_2 .

crystallization, time-dependent changes in materials properties during bond processing and cell operation, sidewall and cell insulation stresses, and possible stress relief mechanisms such as creep, microcracking, or localized bond failure.

Cements

Cements were developed at PNL for bonding graphite to various TiB_2 -based coatings. A patent application is being filed for these cements. Cathodes fabricated from these cements withstood laboratory-scale, short-duration electrolysis tests with no indication of coating/substrate separation. However, these tests resulted in bond/graphite substrate degradation at surfaces contacting aluminum and cryolite bath. This degradation is believed to be caused by Al_4C_3 formation and subsequent dissolution into the aluminum and/or cryolite bath (Hollingshead and Brown 1981; Dorward 1973a and 1973b; Grjotheim, Naeumann, and Oye 1977; Dewing 1969 and 1974). To use these cements for commercial Hall-Heroult cell retrofit applications, it will be necessary to protect the cements and graphite substrates from erosive chemical reactions with aluminum or cryolite bath. In addition, deformation of carbon cell bottom materials, caused by sodium intercalation and salt crystallization (Waddington 1963; Sorlie and Oye 1984; Panebianco and Bacchiega 1966; Dell 1967 and 1985; Dewing 1963 and 1974), is expected to impair the long-term adhesion of these bonds.

Figure 78 illustrates an electrolysis test cathode of Great Lakes TiB_2 -graphite composite material (TiB_2 -G) bonded to Union Carbide Type 1370 graphite using the cement. Electrolysis tests were performed with inert anodes in a laboratory-scale cell for 8 h using a cathode current density of 1 A/cm^2 . As indicated in Figure 78, the bond was maintained during electrolysis; however, some degradation of the graphite substrate and bond layer was evident at the bath contacting surfaces. An aluminum film, evident at the outer periphery of the bond layer and covering the exterior surfaces of the TiB_2 -G, suggests that the observed deterioration may be caused by the formation and subsequent dissolution of Al_4C_3 . The deteriorated regions were also believed to have been attacked by cryolite in this experiment, because an aluminum pad was not introduced prior to electrolysis.

FIGURE 78. Polished Surface of Electrolysis Test Cathode: Great Lakes TiB_2 -Graphite Composite Bonded to Union Carbide Type 1370 Graphite Using Cement. Degradation is indicated by bath penetration at the bond surface (right).

The same bonded material was soak tested in aluminum contained in Al_2O_3 crucibles, without cryolite present, at 970°C in a flowing argon atmosphere (99.9% pure) for 2- and 7-wk periods. A metallographic examination indicated extensive deterioration of the graphite substrates and cement layers within 2 wk. No further analysis was performed on the samples. It is plausible that Al_4C_3 formation is responsible for the attack, based on the free energy of formation from elemental aluminum and carbon.

Figure 79 illustrates a TiB_2 coating that was cemented to graphite. Electrolysis testing of cermet anodes in a laboratory-scale cell indicated features of degradation similar to those of the TiB_2 -G materials bonded to graphite with the cement in Figure 78. Samples of TiB_2 bonded to graphite using the cement were soak tested in molten aluminum for 2 and 7 wk. These tests were performed in Al_2O_3 crucibles with no cryolite present at 970°C under a flowing Ar atmosphere. Extensive degradation of graphite and bonds was observed within 2 wk. No further chemical analysis was performed. As before, it is plausible that Al_4C_3 formation is responsible for this attack, based on the free energy of formation from elemental aluminum and carbon.

FIGURE 79. Polished Surface of TiB_2 Bonded to Poco Graphite Type AXF-5Q Using Cement

Coatings of TiB_2 + 1% copper and TiB_2 + 1% nickel were also successfully bonded to graphite using the cement. Copper and nickel were originally used as TiB_2 sintering aids. Soak tests were performed in molten aluminum using these samples and extensive intergranular penetration of TiB_2 by aluminum was observed during soak tests. These tests were performed in aluminum contained in Al_2O_3 crucibles with no cryolite present at 970°C for 2 wk in a flowing argon atmosphere. Phase separation was also prevalent throughout the aluminum

penetrating the TiB_2 in these samples; this phase separation is believed to have been caused by copper aluminide or nickel aluminide formation (Hansen and Anderko 1958; Finch and Tennery 1982; Kubaschewski and Heymer 1960).

TiB_2 -AlN Materials Bonded to Graphite

Composite tiles were made of graphite substrates coated with a layer of 50 vol% TiB_2 • 50 vol% AlN; the tiles were subsequently evaluated in 1) short-duration laboratory-scale electrolysis tests with cermet anodes, and 2) soak tests in molten aluminum. These tests were intended to evaluate the feasibility of Kaplan's proposed method of building commercial cells by cementing the graphite substrates of the tiles directly on to prebaked carbonaceous cell bottoms (Kaplan et al. 1982). The primary result from the electrolysis and soak tests was that the coatings appear to be resistant to chemical attack; however, the graphite substrates exhibit chemical erosion at regions contacting molten aluminum or cryolite. Based on these results, it is expected that usage in commercial cells may result in coating detachment unless suitable methods are developed for protecting the graphite substrates from chemical attack by aluminum or cryolite bath.

Fabrication methods used at PNL for these tiles were based on the patent by Kaplan et al. (1982) and involved use of a single hot pressing step to densify 50 vol% TiB_2 • 50 vol% AlN powder mixtures and simultaneously bond these coatings to graphite substrates. Specifically, 5 x 5 cm tiles were fabricated by hot pressing 1:1 volumetric mixtures of AlN powder^(a) and carbothermically reduced TiB_2 powder^(b) onto graphite substrates using 5000 psi die pressure at 1850°C for 30 min under a flowing argon atmosphere. Kaplan et al. (1982) suggested that mechanical bonding between the graphite and the TiB_2 • AlN coating is achieved by powder penetration and subsequent densification inside the rough surface pores of the graphite. Evidence for this penetration appears in Figure 77.

Short-duration electrolysis tests with 50 vol% TiB_2 • 50 vol% AlN bonded to graphite in the 1-A cell indicated excellent resistance of the coatings to

(a) TiB_2 powders are 1 to 5 μm in diameter. Aremco Corp., Ossining, New York.

(b) AlN powders are -325 mesh. Aremco Corp., Ossining, New York.

chemical attack by the cryolite bath or aluminum. However, chemical erosion of graphite substrates was observed at surfaces contacting the aluminum or cryolite bath (Figure 80). Electrolysis tests were performed with inert anodes in 1-A cells for 8 h using a cathode current density of 1 A/cm^2 . Soak tests, which were conducted in molten aluminum contained in Al_2O_3 crucibles with no cryolite present at 970°C for 2 to 7 wk under a flowing argon atmosphere, also indicated excellent resistance of the TiB_2 -AlN coatings to aluminum attack. However, extensive degradation of bonds and graphite substrates was observed during the soak test. No further chemical analysis was performed to confirm the cause of the attack on the graphite; however, it is plausible that Al_4C_3 formation is responsible, based on the free energy of formation from elemental aluminum and carbon. Based on the soak and electrolysis tests, it is expected that usage in commercial Hall-Heroult cells may result in coating detachment unless suitable methods are developed for protecting graphite substrates from chemical attack. Furthermore, it is suggested that dimensional instabilities

FIGURE 80. Electrolysis Test Cathode: Polished Surface 50 vol% TiB_2 · 50 vol% AlN Bonded to Union Carbide 1370 Graphite. Chemical erosion of graphite substrate appears at the bath contacting surface.

from sodium intercalation and salt crystallization in carbon-based cell bottom materials may impair alignment of anode/cathode spacing and possibly the bond integrity of these composite tiles.

Additional experiments were performed to determine if improvements in the bonding of $\text{TiB}_2 \cdot \text{AlN}$ coatings to graphite could be made by enhancing the degree of powder impregnation into the surface pores of the graphite. The following experimental procedures were used to enhance entry of powders into the graphite surface pores: 1) graphite substrates were ultrasonically cleaned in isopropyl alcohol to remove microscopic particles of graphite that are poorly attached to machined surfaces (Mullendore and Smatana 1985), 2) a methanol-based suspension containing a 1:1 volumetric mixture of TiB_2 and AlN powders was applied to the cleaned surfaces of the graphite with a paintbrush; the powders in the suspension deposited onto the graphite by the capillary absorption of methanol into the porous graphite, and 3) a dry mixture of TiB_2 and AlN powders having 1:1 volumetric proportion was then placed on top of this coating, and a composite tile was hot pressed using the aforementioned procedure.

After hot pressing, the coatings were not attached to the graphite substrates. The undersides of the coatings exhibited a thin layer of loose powder that could easily be removed by scraping with a knifeblade. Immediately adjacent to this layer, the removed coating of $\text{TiB}_2 \cdot \text{AlN}$ exhibited more dense material that could not be abraded with the knifeblade. Identical graphite samples, coated with the TiB_2 -AlN-methanol suspension, were pressureless sintered beside the hot press die in the same experiment. These coatings were entirely composed of loose powders after sintering. Based on these results, it is suggested that bonding to graphite may be improved by enhancing densification kinetics within the impregnated pore spaces. The lack of densification directly adjacent to the graphite in the hot pressed sample may be attributed to locally reduced compressive stresses exerted on the powders situated in the surface pores of the graphite. Enhancing densification kinetics may be achieved by various methods, such as increasing the die pressure, increasing the sintering temperature, reducing the average particle size, chemically pretreating powder surfaces, using sintering aids and/or high-purity TiB_2

powder (Hoekje 1981; Baumgartner and Steiger 1984; Baumgartner 1984a; Finch et al. 1986; Culbertson and Mathers 1981; Trontelj and Kolar 1973; Takatsu and Ishimatsu 1981; and several additional references in Pastor 1977).

Soak Tests of TiB_2 and TiB_2 -AlN Composites

Soak tests in molten aluminum were performed to investigate reactions with TiB_2 and TiB_2 -AlN samples. Samples of TiB_2 and 50 vol% TiB_2 -50 vol% AlN were hot pressed at 1850°C for 30 min under 5000 psi die pressure and a flowing argon atmosphere; carbothermically reduced TiB_2 powder was used in these experiments.^(a) All samples were individually soaked in aluminum contained in alumina crucibles with no cryolite present at 970°C for 1 to 7 wk under a flowing Ar atmosphere. Figure 81 shows extensive intergranular penetration of TiB_2 by aluminum after 2 wk; similar effects were observed in the 7-wk soak test samples of TiB_2 . In contrast, exceptional resistance to attack by aluminum was indicated in the samples containing AlN (Figure 82) for both the 1-wk and 7-wk soak tests. Scanning electron microscopy of polished surfaces of TiB_2 -AlN soak test specimens revealed penetration of an unidentified phase at TiB_2 grain boundaries (Figure 83). This phase was concentrated within a 100- μm layer directly adjacent to the aluminum reservoir interface. Energy dispersive spectroscopy analysis indicated trace amounts of aluminum and tungsten in this phase. Tungsten is likely to have originated from the wearing of tungsten carbide balls during ball milling of TiB_2 and AlN powders prior to sintering. The impact of this tungsten on test sample performance is not known.

Although several authors report exceptionally good resistance of TiB_2 -AlN composites to attack by molten aluminum (Richards, Berry, and Johnston 1967 and 1968; Kaplan et al. 1982; Meyer 1983; Zdaniewski 1985), it is not clearly understood why these materials, which are made of carbothermically reduced TiB_2 powder, exhibit superior performance over single-phase polycrystalline TiB_2 produced from the same powder. AlN may form a stable oxynitride phase, which may contribute to the resistance to aluminum attack (Boxall, Cooke, and Hayden 1984; McCauley and Corbin 1979).

(a) TiB_2 powders are 1 to 5 μm in diameter. AlN powders are -325 mesh. Both powders were supplied by Aremco Corp., Ossining, New York.

FIGURE 81. Aluminum Soak Test Specimen: Polished Surface of TiB_2 Hot Pressed from Carbothermically Reduced Powder. TiB_2 intergranular penetration by molten aluminum is observed throughout the sample.

FIGURE 82. Polished Surface of Molten Aluminum Soak Test Specimen: 50 vol% TiB₂ · 50 vol% AlN. Exceptional wear resistance is indicated with no evidence of microcracking or grain spalling after 1 wk of exposure to aluminum at 970°C.

In contrast, close control over composition is required to prevent sometimes catastrophic intergranular penetration by molten aluminum in sintered single-phase polycrystalline TiB₂ prepared from carbothermally reduced powder without AlN additions (Ransley 1962 and 1963; Dorward 1982 and 1983; Dorward and Payne 1983; Meyer 1983; Zdaniewski 1985). In these materials, Zdaniewski (1985) reported that microsegregation of impurities at TiB₂ grain boundaries significantly influences intergranular penetration rates and the mechanism of stress corrosion cracking in molten aluminum environments. Intergranular penetration in single-phase polycrystalline TiB₂ may be alleviated by sintering high purity powder, such as that produced from halide vapor reduction processes (Hoekje 1981; Baumgartner 1984a and 1984b). It is interesting to note that these high-purity powders may also exhibit enhanced densification kinetics relative to carbothermally reduced TiB₂ (Hoekje 1981; Baumgartner and Steiger 1984; Baumgartner 1984a; Finch et al. 1986). If TiB₂-AlN or high-purity TiB₂ materials are eventually used for commercial cell cathodes, it is recommended

FIGURE 83. Backscattered Electron Images of Polished Surfaces of 50 vol% TiB_2 • 50 vol% AlN Before and After Soak Testing in Aluminum for 1 wk. AlN is the dark-colored phase. An unidentified phase, containing aluminum and tungsten, appears at TiB_2 grain boundaries after the soak test.

that future research focus on characterization of grain boundary microsegregation processes, which significantly control the resistance to attack by aluminum.

Great Lakes TiB_2 -Graphite Replaceable Cathode

Cell designs were evaluated at PNL using replaceable TiB_2 -G Type B cathode fixtures. Similar designs have been reported by Goodnow and Payne (1982), whereby cathodes are set in place, but not rigidly affixed to the cell bottoms. Short-term electrolysis experiments with cermet anodes in 1-A and 60-A cells indicated that these design concepts are feasible for evaluation of larger cells without requiring major retrofit modifications to existing commercial cell designs.

Electrolysis experiments were performed with cermet anodes and focused on evaluation of $\text{TiB}_2\text{-G}$ Type B monoliths that were loosely set into place in slots in the carbon cell bottom material (Figure 84). Uninterrupted current flow was maintained during 40 h of electrolysis in 1-A and 60-A cells with inert anodes. After sectioning for metallography, the $\text{TiB}_2\text{-G}$ monoliths were intact, and aluminum films were observed wetting all sides of the monoliths. Based on these results, scale-up studies appear feasible for $\text{TiB}_2\text{-G}$ drained cathode design concepts. In addition, these materials have good wear resistance and attractive shape fabricability for commercial cell retrofit applications (Tucker et al. 1986).

Although replaceable drained cathode fixtures have several attractive features, dimensional instabilities in carbonaceous cell bottom materials are

FIGURE 84. Laboratory Scale Hall-Heroult Cell with $\text{TiB}_2\text{-G}$ Replaceable Cathode Module

expected to misalign the anode and cathode due to sodium intercalation and salt crystallization over extended periods of time. This problem may be alleviated by using graphite instead of prebaked carbon blocks to line the floor of commercial cells. It is also recommended that additional research focus on the development of mechanical spacers that can be attached to anode-cathode surfaces to fix the interpolar spacing. Examples of promising design concepts for monopolar and bipolar electrodes have been proposed by Jarrett and Hornack (1985); small-scale electrolysis tests will be performed on these design concepts in FY87.

Additional studies were performed to evaluate the wear behavior of TiB_2 -G cathode materials with and without a molten aluminum pad at the beginning of electrolysis. As indicated in Figure 85, TiB_2 -G Type B cathodes exhibited improved wear behavior in electrolysis tests that were started with an aluminum pad in place; these materials showed no microcracking or spalling after the test. In contrast, TiB_2 grain spalling was observed in all previous PNL electrolysis tests that lacked a pre-existing aluminum pad to protect the TiB_2 -G cathodes from cryolite attack. Substitution of graphite by aluminum within TiB_2 pores at the outer periphery of cathodes has been consistently observed in TiB_2 -G cathodes electrolysis tested with inert anodes at PNL. For example, Figure 85 indicates that, at the anode facing surface, a layer of graphite has been removed from the pores of the TiB_2 to a depth of approximately 200 μm ; this result will be compared to the results of longer duration tests to be performed in FY87.

Elemental mapping from x-ray spectroscopy was used to evaluate reaction zones in a TiB_2 -G Type B cathode that underwent 40 h of electrolysis with a cermet anode. We evaluated the polished surface appearing in Figure 85, where an aluminum pad was not used at the beginning of electrolysis to protect the cathode from attack by cryolite. The results of this study (Figure 86) confirm that a thin layer of molten aluminum replaces the graphite within the pores of the TiB_2 at the periphery of the cathode. The results also indicate that sodium, aluminum, and fluorine (not shown) penetrate the pores of the TiB_2 directly beneath this peripheral layer of aluminum, suggesting the presence of cryolite bath. In addition, sodium, aluminum, and fluorine were detected

FIGURE 85. Polished Surfaces of $\text{TiB}_2\text{-G}$ Replaceable Cathodes After 40-h Electrolysis with a Cermet Anode. Molten aluminum penetrates the pores of the TiB_2 at the edges of both specimens. The absence of an aluminum pad at the beginning of electrolysis results in spalling of TiB_2 grains that become entrained in the aluminum generated during electrolysis.

throughout the graphite phase at randomly evaluated regions in the polished surface, suggesting penetration of electrolyte constituents into the center of the sample. Small amounts of iron and nickel were observed in the aluminum coating the cathode; these elements are expected to be wear products from the cermet anode.

Soak Tests of $\text{TiB}_2\text{-Graphite}$ Composites

$\text{TiB}_2\text{-G}$ Type A and B samples were soak tested in aluminum contained in Al_2O_3 crucibles with no cryolite present under an argon atmosphere at 970°C for 1 to 7 wk to duplicate the effect of no cathodic protection on cathode performance. These samples exhibited aluminum-filled cracks, spalled grains of TiB_2 , and extensive depletion of graphite from aluminum-carbon reactions

FIGURE 86. Elemental Dot Map of Polished Section of TiB₂-G Replaceable Cathode Module After 40 h of Electrolysis. Spalling of TiB₂ grains is shown; however, this is not expected to occur when an aluminum pad is present in the cell previous to electrolysis. Iron and nickel are seen in the outer film of aluminum; these phases may be wear products from the anode.

(Figure 87). There was no difference in the soak test performance of $\text{TiB}_2\text{-G}$ Type A and B materials, based on observations from optical metallography.

Differences between the soak test results and the successful performance of $\text{TiB}_2\text{-G}$ during electrolysis testing are not clearly understood at the present

FIGURE 87. Polished Surfaces of $\text{TiB}_2\text{-G}$ Type B Before and After Soaking in Aluminum for 1 wk, Showing Microcracking. Faceted crystals (below right) have not been positively identified, but may be Al_4C_3 , based on the free energy of formation from elemental aluminum and carbon at 970°C .

time. These differences may be attributed to the following hypothesis. Oxidizing conditions at the anode during electrolysis favor depletion of Al_4C_3 from the bath, which may then enable diffusion of Al_4C_3 from aluminum-graphite interfaces through the aluminum and into the bath. During soak testing, it is possible that molten aluminum becomes saturated with Al_4C_3 , based on the molar volumes of molten aluminum and carbon present in these experiments. Therefore, as the aluminum becomes saturated with Al_4C_3 during one of these soak tests, Al_4C_3 dissolution rates at aluminum-graphite interfaces should diminish with time. Meanwhile, the cracks in the TiB_2 network may have formed as a result of the volume expansion of Al_4C_3 forming within the pores of the TiB_2 . This is possible, considering that 1 cm^3 of graphite is required to form 3.8 cm^3 of Al_4C_3 . To evaluate this hypothesis, additional testing will be performed in FY87.

Coatings Produced by Sintering

Experiments were performed to determine the feasibility of producing TiB_2 and ZrB_2 coatings on graphite by way of a sintering process (Figure 88). A patent application is being filed for this coating process.

The coatings produced do not appear to be feasible for Hall-Heroult cell cathodes because the coating porosity should result in the deterioration of graphite substrates by way of penetration of bath or molten aluminum. It may be possible to reduce the porosity of the coatings. Possible alternatives for enhancing densification kinetics include usage of carbon additives and/or high purity powder (Baumgartner and Steiger 1984; Baumgartner 1984a; Finch et al. 1986; Pastor 1977). If these or other methods can be used to form durable thin coatings, these materials might be economical if employed in replaceable cathode fixtures, which are exchanged from a hot cell after a finite wear period.

Other Accomplishments

Based on experimental research performed at PNL in FY86, the following invention reports have been filed:

1. "Method of Bonding TiB_2 -based Coatings to Graphite," by C. H. Schilling and N. C. Davis.

FIGURE 88. Sintered Coatings of TiB₂ and ZrB₂ on Graphite

2. "Method of Applying Refractory Hard Material Coatings," by C. H. Schilling and S. C. Marschman.
3. "Fabrication Methods for the Production of Inert Bi-Polar Electrodes for Use in the Electrolytic Production of Metals," by S. C. Marschman and C. H. Schilling.

FUTURE DIRECTIONS

Laboratory-scale electrolysis tests with inert anodes will be performed in FY87 to evaluate two main cell design concepts: 1) replaceable cathode fixtures using TiB₂-based monoliths that are set in place on carbon cell bottoms without being rigidly attached, and 2) replaceable anode/cathode fixtures using mechanical spacers to fix interpolar spacings. Additional experiments will be

performed to evaluate wear mechanisms in inert spacer and cathode materials. Based on this research, design recommendations will be made for scale-up to a pilot cell.

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SENSOR DEVELOPMENT

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The objective of the Sensor Development Task is to develop sensors that will be used in the control of the bath chemistry of Hall-Heroult cells using stable anodes and cathodes.

SUMMARY

The work conducted by the Sensor Development Task in FY86 consisted of two major efforts: development of methods and equipment for measuring liquidus temperature and development of sensors for determining the electrolytic conductivity of molten cryolite.

Three methods for successfully measuring the liquidus temperature of molten cryolite without contacting the cryolite were demonstrated. Each of the methods uses a distinctly different system for detecting the presence of solids on the molten cryolite. These systems include:

- an infrared imager
- a spectrum analyzer
- a combined radiometer, pyrometer, and laser.

Accomplishments in the development of sensors for determining the electrolytic conductivity of molten cryolite included the following:

- development of two- and four-electrode conductivity probes for short-term use
- evaluation of commercially available systems for measuring conductivity without contacting the cryolite.

The conductivity probes worked successfully in short-term tests; long-term tests are planned. Extensive development work would still be needed to develop reliable noncontact methods of measuring conductivity.

TECHNICAL PROGRESS

To describe this task's two major areas of development, the technical progress section is divided into two sections: determination of liquidus temperature and measurement of the electrolytic conductivity of molten cryolite.

Methods for Determining the Liquidus Temperature of Cryolite

The liquidus temperature is the maximum temperature at which both solid and liquid phases are present in the cryolite bath. This temperature is strongly affected by both the concentration of alumina and the ratio of NaF to AlF_3 (bath ratio or cryolite ratio) in the bath. Since the bath ratio is relatively constant, the determination of a liquidus temperature would, in effect, be a determination of alumina concentration.

Three different types of instrumentation systems have been studied for the purpose of developing a non-contact method for determining the liquidus temperature of a cryolite-alumina melt. All three systems appear to be capable of determining liquidus temperature. None of the three systems requires immersion into or contact with the melt. The first system discussed is a combination of a radiometer, a pyrometer, and a laser. The second is a fast analyzer of spectral energy distribution in the 400- to 1070-nm range. The third is an infrared imager operating in the 8000- to 14,000-nm range. A means for cooling a small portion of the melt surface to induce formation of a thin solid crust is required in all cases. A heat pipe or a flow of cool, inert gas can be used to induce this formation.

The radiometer-pyrometer-laser system is preferred for continuous monitoring of the melt in many tanks simultaneously. It can be used as a monitor for an automatic process control system.

The spectrum analyzer provides more detailed spectral information, senses the formation of the solid film, and may be useful for developing other methods of melt monitoring.

The infrared imager is the most easily applied for spot testing where continuous monitoring of many tanks simultaneously is not required. The liquidus temperature is directly determined by reading the temperature of the transition zone between the solid crust and the liquid.

The Radiometer-Pyrometer-Laser Liquidus Temperature Measurement System

A radiation pyrometer can function as a liquidus-temperature sensor, if it is provided with a means for determining that a film of solid material is present on the surface of the cryolite bath. In an operating aluminum electro-winning process, the surface of the bath is normally hot enough to be free of solids. With no solids on its surface, the bath is somewhat transparent, a fact that affects the temperature registered by a radiation pyrometer. The surface can be locally cooled using a jet of cool inert gas or possibly a heat pipe. When the cooled surface reaches liquidus temperature, a film of solid material will begin to form. Initially this film is thin and in very good thermal contact with the liquid beneath it. With the film on the surface, the pyrometer sees only the surface and therefore may be expected to give an accurate value for the liquidus temperature.

In the experiments described below, the bath surface was cooled primarily by letting the whole bath cool. At times, a jet of argon was used to stimulate the formation of the film while the bath was still above liquidus temperature. The main emphasis of these experiments was on defining a film sensing method.

The method used in detecting the film is illustrated in Figure 89. A collimated beam of light from a small helium-neon laser was directed at the surface of the cryolite bath. When the surface was clean and free of a film of solid material, nearly all of the light was reflected in the specular direction and only a very small portion of it reached the radiometer. There was essentially no scattered light and the radiometer reading was low. As the cryolite was allowed to cool, the surface, being the coolest, reached liquidus temperature first and a thin film of solid material formed on the surface. This solid material does not have a smooth specular surface. It therefore scattered light in all directions as indicated by the oval shown in Figure 89. This generated a high reading on the radiometer. With a high reading, the presence of film is indicated and the pyrometer reading can be taken as the liquidus temperature.

Since the bath temperature is well above 900°C, it is radiating strongly in the spectral acceptance band of the radiometer. A narrow pass band optical filter was used to restrict the spectral acceptance band of the radiometer to the region of the laser output at 632.8 nm. Even in this narrow passband, the

FIGURE 89. Method for Detecting Formation of Solid Film

energy radiating from the cryolite overpowered the response of the radiometer to scattered laser light so a chopper was used to modulate the laser beam. Figure 90 provides information about the equipment used in the experiment. Using a lock-in amplifier synchronized to the chopper frequency (5000 Hz), all the effects of the radiant output of the cryolite upon the radiometer were nullified and the output of the lock-in amplifier became a function of the scattered modulated light only.

Figure 91 shows the results of an experiment in which the cryolite bath was cooling and a solid film was forming. At the left, the recorded signal level is about 90 millivolts (mV), corresponding to a clean liquid surface. As a film is formed on the surface, the signal rises to 320 mV at which time an alumina rod is used to sweep the surface clean. The presence of the rod in the field during the stirring generates excursions in the record, but the chief

FIGURE 90. Instrumentation for Measurement of Liquidus Temperature

effect is the return of the signal to the low (90 mV) state, indicating that all of the film has been removed. With time, the film again forms and the signal rises to 175 mV. Each time the surface is cleaned, the signal drops to 90 mV; and each time a film forms, it rises. With continued cooling and the surface left undisturbed, the signal will rise to 450 mV.

Noise on the record can be diminished by increasing the time over which the signal is integrated. Integration time can be selected by means of a switch on the lock-in amplifier. The integration time in Figure 91 is initially 0.1 sec but was changed to 1 sec at approximately 9.5 min. The longer integration time greatly reduces system noise and provides an adequate response time for control. Figure 92 shows the curves redrawn without the noise for greater clarity.

FIGURE 91. Radiometer Signal Record

The data presented in Figures 91 and 92 show that the radiometer-pyrometer-laser method used and defined by Figure 90 clearly detects the presence or absence of a solid film on the surface of a cryolite melt. Also, the thickness of the film can be judged by the level of radiometer response, as indicated by the slope of the film formation part of the record. With further work, the response could be calibrated in terms of film thickness.

A system designed for use in an aluminum production facility need not be as complex as the system used in the experiment and shown in Figure 90. The functions of the radiometer and pyrometer can be combined in one unit. A radiation pyrometer may be defined as a radiometer used in combination with signal processing electronics which interpret the radiometer signal in terms of temperature. The resulting schematic for the combined system is shown in Figure 93. The radiometer output goes to both a lock-in amplifier and to the pyrometer electronics. The lock-in amplifier verifies the presence of a film of a certain thickness on the surface of the cryolite. Cool inert gas is piped

FIGURE 92. Radiometer Signal Record from Figure 91 with Noise Removed

into the enclosure. The flowing gas exits the enclosure at the surface of the cryolite, cooling the surface and causing a solid film to form. When film presence is verified, the chopper is positioned to cut off the laser beam, and the pyrometer electronics begin to interpret the radiometer output as a temperature. Output signals from the pyrometer electronics can be displayed, recorded, and used to control the aluminum electrowinning process.

The cryolite melt radiates much like a black body as is illustrated in Figure 94. Figure 94 shows the spectral radiance of a cryolite melt at 945°C. The ratio of the radiance at any given wavelength to that at 1062 nm is plotted as a shaded region. This ratio is compared with the same ratio for a black body referenced to 1.07 μm (1070 nm) which is plotted as a single line. The melt temperature was measured using a thermocouple immersed in the melt. Similar tests show that the radiation characteristics of the melt capped with a solid film are also like that of a black body.

FIGURE 93. Liquidus-Temperature Measurement Device Concept

Three types of radiation pyrometers may be defined: 1) total, 2) single color, and 3) two color (also called "ratio"). The first two types assign a temperature on the basis of the total radiance within the spectral acceptance band of the pyrometer. That acceptance band is quite broad for the total radiation pyrometer and quite narrow for the single-color pyrometer. For both of these types, a knowledge of the emittance of the material is required if the true temperature must be known.

By calculating the ratio of radiances in two different spectral bands, a "true" temperature can be calculated without knowledge of the emittance if it is assumed that, whatever the emittance is, it is the same in both spectral bands.

$$100\% = 6.910E^{-01} \text{ W/sr/m}^2$$

Peak at 1070 nm

FIGURE 94. Comparison of Spectral Radiance of Cryolite to Radiance of a Black Body

In practice, the single color pyrometer is usually more reliable and effective because the assumption upon which the ratio pyrometer operates is not true for many materials and the exactness to which the emittance must be known for reliable use of a single-color pyrometer is not high. The indicated temperature is much more strongly dependent upon the radiance within the spectral acceptance band than upon the emittance in the same band. For these reasons, it is anticipated that single-color pyrometry will be the most suitable type to use in the liquidus-temperature measurement system. To implement the system shown in Figure 93 the spectral output of the laser or other light source must be strong within the spectral acceptance band of the radiometer. The light source need not be a laser. A tungsten-filament incandescent lamp imaged upon the bath surface would probably work just as well. The specularly reflected light should be absorbed within the enclosure as implied by the pointed shape of one arm of the enclosure shown in Figure 93. To avoid errors in temperature measurement, the light source should be blocked during the temperature measurement part of the cycle before it enters the enclosure.

The Spectral Reflectance System

A Photo Research spectro-photometer^(a) was used to study the radiation characteristics of the cryolite melt surface both with and without a solid film present. Accurate comparisons of the surface in different conditions could be made by storing a reference spectra in memory and dividing other spectral responses taken under different conditions by the reference. Figure 95 shows the arrangement used in taking the data. A microscope lamp was used to illuminate the surface of the cryolite. When the surface of the cryolite melt was

FIGURE 95. Experimental Arrangement for Tests Using a Spectral Radiometer

(a) Photo Research 700 Series Spectrascan;® Photo Research is a division Collmorgen Corp.

clean and clear, very little of the illuminating light was scattered to the radiometer head; but when a film formed on the surface, light was scattered, altering the recorded spectra.

Figure 96 is a printout of the spectra generated by a clean melt surface. Nearly all of the energy seen by the radiometer head is due to the thermal radiation of the cryolite. Figure 96 shows a spectrometer printout with superimposed black body curves for various temperatures. The melt temperature, as indicated by a thermocouple immersed in the bath, was 945°C. The printout also includes the values of several quantities calculated by the spectrometer including the radiance in the spectral band from 390 to 1070 nm, the luminance, the C.I.E.^(a) chromaticity coordinates, and, when appropriate, the color temperature of the radiation. A comparison of the spectro-photometer printout

100% = $7.281 \text{ E}^{-01} \text{ W/sr/m}^2$

Peak at 1070 nm

FIGURE 96. Spectral Radiance Distribution of a Clean Cryolite Melt Surface at 945°C

(a) Commission Internationale d L' Eclairage.

with the equivalent curve for a 945°C black body shows that the spectral radiance of the cryolite melt approximates that of a black body of the same temperature.

Figure 96 also illustrates the strong predominance of infrared in the radiation. This prevented the calculation of good ratios in the blue end of the spectrum. To alleviate this problem, an infrared blocking filter was placed in the system (Figure 95). The spectral radiance plot of a 941°C clean cryolite melt surface, modified by the filter, is shown in Figure 97. This was used as the reference spectra. The melt was allowed to cool to 927°C by which time a film of solid covered the surface. Figure 98 shows the corresponding spectral plot. Comparison with Figure 97 shows that the solid film produces a surface richer in the blue (short wavelength) end of the spectrum. The energy output of the microscope lamp, operating at ~3000°C, is much richer in blue light than the cryolite at 927°C. When the solid film forms, this blue-rich light is scattered into the direction of the radiometer head. Dividing the

FIGURE 97. Energy Spectrum of 942°C Melt Surface Viewed Through Infrared Blocking Filter (Reference Spectrum)

Peak at 682 nm

FIGURE 98. Energy Spectrum of 927°C Solid Film Over Cryolite Viewed Through Infrared Blocking Filter (Test Spectrum)

927°C spectra by the reference spectra, the plot of Figure 99 was obtained. The formation of the film of solid material is readily detected by the buildup of the spectral energy in the 400- to 500-nm region providing that the illuminating light source is richer than the radiation from the cryolite in this spectral band. If, on the other hand, a helium-neon laser had been used as a light source, the buildup of the solid film would have generated a spike in the ratio at 632.8 nm.

A spectro-photometer of the type used for this study, while not being directly applicable for continuous monitoring of liquidus temperature, could be used for spot checks of the melt condition. A reference spectrum of the clear melt surface would be taken and stored in the system memory. The formation of a thin solid film would be induced on a small area of the surface of the melt using a heat pipe or a flow of cool inert gas. A second reflectance spectrum would be taken with the surface illuminated by a tungsten lamp. The reference spectrum would be divided by the film reflectance spectrum. If film presence

Peak at 426 nm

FIGURE 99. Ratio of Spectra - Test/Reference

was confirmed by a blue-rich ratio spectrum, the liquidus temperature would be determined by the radiance computed for the film spectrum. This radiance figure is automatically provided by the spectro-photometer display.

The Infrared Imaging System

Recent improvements in commercially available infrared imagers make them a powerful tool for the study of temperature distributions. A molten cryolite surface was studied using an Inframetrics 600 L imager. Similar imagers using mercury-cadmium-telluride detectors are available from Hughes Aircraft Co., UTI Instruments Co., and AGA Corp. Other systems based on pyroelectric detectors are available from I.S.I. Group Inc. and Xedar Corp. One piece of information immediately gathered from this study was that the emittance of liquid cryolite when viewed through a clean surface is very nearly equal to 1.0; that is, it is a near perfect radiator in the 8- to 14- μ m spectral range. An emittance of 0.97 was measured while viewing the liquid cryolite through a mirror. Measurements were made by adjusting the emittance setting on the instrument until the

temperature it reported coincided with that given by a thermocouple placed in the graphite container holding the cryolite.

When a solid first begins to form on the clear liquid surface, it will at times build up in a uniform manner, making it difficult to detect using the imager. As the film builds up in thickness, it appears to break up, forming something like an assembly of floating ice blocks. This condition is easily identified in the infrared image.

Solid material forming in the liquid surface was observed to have an apparent temperature as much as 50°C cooler than the liquid. This difference in observed temperature is due, at least in part, to a difference in emittance. It is likely that any solid film formed will be in thermal equilibrium with the liquid beneath it and at the same temperature as the surface of the liquid.

The infrared images generated during the experiment were recorded on video tape. Color photos of the cryolite were later made using the video tape to recreate the images. It is believed that a liquidus temperature can be directly read from the infrared imager by positioning the system crosshair on a segment of solid film with the system set for the appropriate emittance factor. More work needs to be done to verify this and determine the repeatability and accuracy of the liquidus temperature determination.

Photographs of two of these infrared images are shown in Figures 100 and 101. Figure 100 shows the infrared image of the cryolite surface with three patches of solid film. In accordance with the technique outlined above, if the cursor were moved over one of these patches and the proper emittance correction made, the instrument would read the liquidus temperature. The cursor, positioned over the liquid as shown, gave a reading of 927°C with an emittance setting of 0.97. In Figure 101, the cursor is positioned over the single large patch of solid film. A temperature of less than 877°C (emittance setting 0.97) was indicated; and this was below the range selected at the time. With the proper emittance setting, the liquidus temperature could have been read.

Liquidus Temperature Sensor Development: Conclusions

The work described above provides a basis for defining a liquidus-temperature measuring instruments for use in improving aluminum production

FIGURE 100. Infrared Image of Cryolite Surface Showing Particle Formation. Three particles present. Temperature at cursor 927°C.

FIGURE 101. Infrared Image of Cryolite Surface Showing a Large Surface Film Particle. Temperature at cursor less than 877°C.

efficiency. The infrared imager could be used directly for spot checks of the liquidus temperature, if some form of liquid surface chiller is provided. It would also be useful as a laboratory tool to develop a better understanding of film formation and the measurement process. The pyrometer-radiometer combination should be developed for applications that require many stations to be

continuously monitored. Prototype instruments should be built, tested, and modified as necessary to define an instrument useful and acceptable to the industry.

Methods for Measuring the Electrolytic Conductivity in Cryolite

Contact and noncontact systems for measuring electrolytic conductivity in molten cryolite baths were evaluated. The apparatus used for testing electrolytic conductivities, and also for determining liquidus temperature, is shown in Figure 102. The noncontact methods tested included commercially available proximity systems based on eddy current coupling.

Noncontact Electrolytic Conductivity Measuring Systems

Several methods for testing bath conductivity without contacting the molten cryolite were reviewed. Different methods, instrumentation used in each method, and possible commercial sources for the instrumentation are listed in Table 7.

The first and second methods described in Table 7 were screened for use as noncontact conductivity measuring devices. The conventional proximity detector in its normal configuration has a 1-MHz typical frequency of operation. It was not sensitive to either the proximity or conductivity of materials that were used to replicate molten cryolite.

The output of a noncontact conductivity sensor is dependent on both distance to the bath and the bath's electrical conductivity. At a sufficiently high frequency, the distance to the bath is the only variable of consequence, but a frequency of 1 GHz is required to resolve the distance to the bath to 10 mils. Lower frequencies give bath penetrations with a subsequent shift in reflected bath impedance from resistive to inductive, as measured by the noncontacting sensing coil or antenna. Measurements at two well-selected frequencies appear to be the minimal requirements for noncontact conductivity measurements.

State-of-the-art eddy current devices have a sensitivity of about 4% IACS (International Annealed Copper Standard). If the value of copper is 1.7 ohm/cm^3 , then the capabilities are on the order of 42 ohm/cm^3 for available devices. Since the value for molten cryolite is about $500,000 \text{ ohm/cm}^3$, eddy

FIGURE 102. Experimental Apparatus

TABLE 7. Noncontact Conductivity Measuring Systems

Method	Equipment	Supplier
Proximity detection	Eddy current-based detectors	Kaman Instruments Corp. Nevada-Bently Co.
	Colpitts oscillator-based detectors	ASI-Keystone Inc. Kaman Instruments Corp. Nevada-Bently Co.
Impedance detection	Slotted toroids	PNL
Nondestructive conductivity testing	Eddy current-based detectors	Nortec Inc.

current devices would have to be improved in sensitivity by a factor of 10,000 over available systems. Additionally, the systems' distance from the bath would have to be minimized since sensitivity would decrease as the distance squared.

If the skin thickness for the proposed cryolite conductivity measurement and the skin thickness implied from the performance limit of available instrumentation are the same, then the frequency of operation will be about 1 GHz. The skin thickness is, however, related to the magnetic permeability frequency product. Therefore, the frequency of operation might be lowered through the use of cobalt materials in the sensor design; Supermendur or a related alloy may be used instead, if cooling of the sensor below the 940°C Curie point is feasible. Under any circumstance, research and development would be necessary in this area because commercially available products do not exist.

A conductivity measurement device based on a Colpitts oscillator and conventionally used in metal detectors was considered. This device was determined inappropriate as a noncontact measuring device because of the change in frequency with distance to the bath, bath conductivity, temperature, search coil and cable characteristics, as well as the interaction with the electric and magnetic field in the bath.

From this study of noncontact methods, we conclude that extensive development work would be required to produce a reliable, noncontact system for measuring conductivity.

Contact Electrolytic Conductivity Measuring Devices

To support in-house inert anode development, our efforts were directed toward the more conventional systems for measuring electrolytic conductivity which use available instrumentation, in direct contact with the bath, to measure conductivity values. The contact methods are commonly referred to as two-electrode, four-electrode, and electrodeless systems. Use of electrodeless instruments is required when electrode impedances or fouling have been shown to limit performance. Evaluation of the two- and four-electrode systems was undertaken first to determine if such problems existed. Tests to date have shown no electrode impedance problems, with either two-electrode or four-electrode probes, that affected accuracy.

Departures from anticipated results have generally been in a direction suggesting shunting of the electrodes. Shunting has been observed to be a result of vapor deposition of conductive material, and diffusion of conductive material into fissures connecting the electrodes. Tests were performed to determine if ionic conduction induced in the boron nitride probe body from exposure to cryolite was a possible shunting mechanism. A two-electrode blind probe was exposed to cryolite for an extended period. No conduction was observed although the probe configuration was similar to a probe under test. This supports the conclusion that the cracking of the boron nitride body is a vapor induced phenomenon. Also, it appears that the deposition of conductive material from the vapor can have a significant effect. An experiment was conducted with a two-electrode probe exposed to a vapor phase and monitored for conduction between the temperatures of 940°C and 540°C. A $1/T$ correspondence with temperature was noted and a 23 kcal/mol activation energy for the conduction mechanism was indicated. The possible correlation of the conductivity of what is presumed to be a deposited film between the electrodes and the bath composition was not pursued.

Electrodeless conductivity was considered only to the point of acquiring and testing the magnetic materials of construction. The only acceptable magnetic material is cobalt which has a Curie point of 1115°C. A powdered cobalt toroid was tested to determine the change in magnetic permeability with temperature. The permeability increased by a factor of six as the temperature

increased from 200°C to 950°C. Magnetic permeability at 950°C is about a factor of 10 lower than conventionally used materials, hence requiring a circuit modification if used with available instrumentation. Further development was delayed to assess the value of the readily available electrode type conductivity instrumentation. Additional work will be performed if the life of the electrode types are unacceptably limited. Salient problems are the sealing of the toroids and windings from exposure to the molten cryolite, and the marginal magnetic properties.

Contact Conductivity Probe Development

The probes consisted of 2 cm- and 2.5 cm-diameter boron nitride rods, which were machined to accept either two or four electrodes and a measurement cell. Table 8 is a listing of the probes tested, with reference to corresponding figures.

The first two-electrode conductivity probe tested, with a cell constant of 57 cm⁻¹, was not an acceptable design for two reasons: 1) fracturing of the gas space body (see Figures 103 through 106) and 2) cell contents not representative of the cryolite bath (i.e., temperature gradient and inadequate molten salt circulation in the cell). Therefore, the two-electrode design was modified to provide better circulation, but at the cost of lowering the cell

TABLE 8. List of Probes Tested

<u>Electrodes</u>	<u>Cell Constant, cm⁻¹</u>	<u>Reference Figures</u>
2, Inconel 600, 1/4 in. or Graphite/Stainless Steel	57	Figures 103 through 106
2, Molybdenum, 1/8 in.	3.35	Figures 107 and 108
2, Molybdenum, 1/8 in.	7.91	Figures 107 and 109
4, Inconel 600, 1/8 in.	0.116	Figures 110 and 111
4, Molybdenum, 1/8 in.	0.121	Figures 110 and 112
4, Tungsten, 1/8 in.	0.124	Figures 110 and 113
4, Molybdenum, 1/8 in.	1.31	Figures 114 and 115
4, Tungsten, 1/8 in.	0.646	Figures 114 and 115
4, Molybdenum, 1/8 in.	0.646	Figures 114 and 115

FIGURE 103. Initial Design of a Two-Electrode Conductivity Probe

constant. This design appeared to be successful for a limited test period of seven hours. Refer to Figures 107, 108, and 109 for construction details.

Four-electrode design is shown in the probes typified in Figures 110 through 113. Performance was close to acceptable for initial short-term use. Shunting, resulting from vapor-phase penetration around the electrode, as well as cracking due to vapor-phase deposition with thermal cycling, was noted. Follow-up designs incorporated features intended to limit these effects. Typical follow-up designs are presented in Figures 114 and 115. The electrode was placed to enlarge the cell constant and limit shunting due to surface films. Cell resistances for each conductivity probe type tested are listed in Table 9.

The following is a list of conclusions and observations concerning the two- and four-electrode conductivity probe tests.

FIGURE 104. Two-Electrode Conductivity Probe. Note gas space fracture and measuring cell break.

FIGURE 105. Two-Electrode Conductivity Probe of 1/4-in. Graphite Bonded
Bonded to 1/8-in. Molybdenum. Boron nitride fiber under clamp.

FIGURE 106. Two-Electrode Conductivity Probe, Split Open. Note gas phase fracture with localized deposit.

1. Electrode impedance was not discernible in either the two- or four-electrode devices. Shunting effects that tend to obscure electrode impedance were dominant (see Figures 103, 107, 110, 114, and 116 through 121).
2. Shunting was the primary mode of poor operation. Pre- and post-run calibrations with HCl disclose that, when shunting occurred, conductivity under prolonged exposure to cryolite was greater than expected. Placing the probe in the vapor space showed a residual conductivity for cracked probes. Post-run tests in HCl and water showed a time signature that indicates cracked if shunting occurred between the electrodes (see Figures 107, 109, and 120).

Body 1 in. Boron Nitride
Electrodes - 1/8 in. Molybdenum
Cell Constant 7.813

FIGURE 107. Final Design of a Two-Electrode Conductivity Probe

3. Cracking of the boron nitride in the vapor-exposed portion predominated. A thermal gradient of 100 to 200°C/in. existed in the portion of the probe above the bath. Vapor phase deposition of conductive material at the boron nitride electrode interface at the cool end of the probe was common. Cracking occurred during both cooling and long-term exposure to the bath. (see Figures 104, 106, and 111).
4. Shunting can be circumvented by avoiding the use of a monolithic probe body and choosing a grade of boron nitride whose temperature expansion more closely matches the metal electrode, or by using smaller diameter electrode leads or a vapor-proof bond between the boron nitride and the electrode (see Figures 111 and 112).
5. The electrodes should be separated with each protected by a heat pipe and spaced to present a constant effective cell geometry. (see Figure 34). Plant conductivity probes need not be monolithic since abundant space is available.

FIGURE 108. Two-Electrode Conductivity Probe with Molybdenum Electrodes, and Slanted Ports. (Ports double cross.)

FIGURE 109. Two-Electrode Conductivity Probe, Final Design

FIGURE 110. Initial Design of a Four-Electrode Conductivity Probe

FUTURE DIRECTIONS

Activities planned for further development of liquidus temperature and electrolytic conductivity measuring methods are outlined below.

Liquidus Temperature

The non-contact methods for measuring liquidus temperature which were tested in FY86 will be further evaluated on the basis of the following criteria:

- accuracy of the measurement
- remotability (hands-off operability)
- adaptability to multiplexing
- cost per bath installation

FIGURE 120. Measurements Taken with a Two-Electrode Molybdenum Conductivity Probe Comparing Temperature and Conductivity Over Several Hours. Cell conditions included a cell constant = 7.81 cm^{-1} , a bath ratio of 1.1, and a conductivity of 2.2 S cm^{-1} .

FIGURE 121. Measurements Taken with a Four-Electrode Tungsten Conductivity Probe Comparing Temperature and Conductivity Over Several Hours. Cell conditions include a cell constant of 0.65 cm⁻¹, a bath ratio of 1.1, and a conductivity of 2.25 S cm⁻¹ at 1000°C.

FIGURE 122. Experimental Apparatus for Measuring the Electrolytic Conductivity of Cryolite

6. Evaluate the following anode dynamic signal analysis methods related to the measurement of cryolite impedance, conductivity, and alumina content.
- A fast Fourier transform (FFT) of the dynamic portion of the cell current and voltage values contains information regarding electrolyte conductivity and capacitive values which can be used to determine alumina concentration.
 - The acoustic output of an inert anode contains amplitude and frequency values that can be related to alumina concentration as well as other process variables.
 - The use of a position sensor for position control of an inert anode coupled with current monitoring as well as cell voltage will be used to develop a method for computing electrolyte conductivity.

Bath Vapor Spectral Analysis

In 1987, we plan to determine if the absorption spectra of bath vapors contain information relatable to bath composition. Required instrumentation will include: 1) a heated chamber through which vapors are drawn, 2) a fiber optic cable for the transmission of source and signal, and 3) a remote absorption spectrograph.

Initial work to substantiate the value of the method will be performed on glass or quartz plates that have been exposed to bath vapors from baths of various compositions. The deposited film will be analyzed for absorption and reflectance characteristics as a function of bath composition. If the initial work is successful, this method will be pursued as time and funding permits.

6. Evaluate the following anode dynamic signal analysis methods related to the measurement of crystal impedance, conductivity, and alumina content.

- A fast Fourier transform (FFT) of the dynamic portion of the cell current and voltage values contains information regarding electrolyte conductivity and capacitive values which can be used to determine alumina concentration.
- The acoustic output of an inert anode contains amplitude and frequency values that can be related to alumina concentration as well as other process variables.
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