18J

Inert Electrode Program

**Laboratory Testing of TiB_2 -Based Cathodes
for Electrolytic Production of Aluminum**

July 1988

**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute**

On the cover:

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

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, or Battelle Memorial Institute.

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE MEMORIAL INSTITUTE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

NTIS Price Codes
Microfiche A01

Printed Copy

Pages	Price Codes
001-025	A02
026-050	A03
051-075	A04
076-100	A05
101-125	A06
126-150	A07
151-175	A08
176-200	A09
201-225	A010
226-250	A011
251-275	A012
276-300	A013

LABORATORY TESTING OF TiB_2 -BASED CATHODES
FOR ELECTROLYTIC PRODUCTION OF ALUMINUM

C. H. Schilling

July 1988

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RL0 1830

Pacific Northwest Laboratory
Richland, Washington 99352

SUMMARY

Experimental research was performed to evaluate TiB_2 -based cathodes, which may be used for retrofitting existing commercial Hall-Heroult cells. Candidate cathode materials and retrofit designs were analyzed in laboratory-scale electrolysis tests and nonpolarized immersion tests in molten Al. The cathode materials and cathode attachment designs were selected based on a literature review (Schilling, Hagen, and Hart 1987) and previous experimental research at the Pacific Northwest Laboratory (Hart et al. 1987). Key results are summarized below:

- The majority of the experiments involved electrolysis testing of replaceable cathodes made of titanium diboride-graphite (TiB_2 -G) composites supplied by the Great Lakes Research Corporation. Electrolysis tests were performed in the laboratory with cermet anodes for time durations of up to 90 h. Based on optical ceramography, most of the cathodes exhibited acceptable performance with no evidence of TiB_2 grain spalling or intergranular penetration by Al. One test showed TiB_2 fragments suspended in Al, which is possibly attributed to chemical attack from alumina (Al_2O_3) supersaturated bath.
- High-resolution optical ceramography and elemental mapping showed molten Al replacing the graphite phase contained within the TiB_2 pores at the surfaces of a TiB_2 -G cathode. Beneath this layer, the TiB_2 pores exhibited a reaction layer that contained Na and F but was depleted of Al and C. Chemical reactions occurring in this layer are likely to control the overall wear resistance of these materials. These results are summarized in a poster which will be published in the American Ceramic Society Bulletin.
- Four types of TiB_2 -based materials were evaluated during non-polarized immersion in molten Al at 970°C with no cryolite (Na_3AlF_6) present under an Ar atmosphere for up to 20 wk. Alcoa high-purity TiB_2 and TiB_2 -AlN composites exhibited superior resistance to chemical attack, with no evidence of fragmentation or

intergranular penetration by Al. Composites of chemical-vapor-infiltrated TiB_2 on ceramic fiber mesh exhibited mixed results; the coatings were resistant to chemical attack, but the fibers reacted with molten Al during the first 4 wk of exposure. The TiB_2 -G composites exhibited damage which may be related to expansion stresses exerted on the TiB_2 pore walls as a result of Al_4C_3 formation. Such stresses are not expected to damage TiB_2 -G materials during electrolysis because of subsurface chemical reactions resulting in the rapid removal of Al_4C_3 from the TiB_2 pores.

- Alcoa high-purity TiB_2 was evaluated as a replaceable cathode in a 140-h laboratory-scale electrolysis test. The cathode exhibited acceptable performance with no evidence of microcracking or penetration by Al, based on optical ceramography analyses.
- A laboratory-scale electrolysis test of a replaceable anode-cathode fixture, which used a BN spacer to mechanically align the anode-cathode spacing, was performed. The anode material performed satisfactorily during 7 h of electrolysis testing, although the spacer was chemically attacked at surfaces exposed to the anode-cathode spacing. Evaluation of wear-resistant spacer materials is recommended.
- A TiB_2 -based paint coating on graphite was evaluated during short-term exposure to molten Al under nonpolarized conditions. The coating was extensively attacked as a result of reactions between the Al and a SiO_2 -based component of the paint coating, and Al_4C_3 formation from reactions between elemental Al and graphite.
- Preliminary experiments were performed to evaluate in situ formation of TiB_2 coatings that may be self-healing in an operating Hall-Heroult cell. The Al-Ti reactions resulted in extensive degradation of Ti during nonpolarized exposure of Ti to B-saturated molten Al. Evaluation of alternative coating methods is recommended, such as electrodeposition and diffusion saturation using molten salts.

- Sintering studies were performed to evaluate whether TiB_2 components can be fabricated with powder prepared by a low-temperature precursor process; the TiB_2 powder was supplied by J. Ritter at the National Bureau of Standards. Samples could not be pressureless sintered to reasonable densities for cathode evaluation studies. Additional studies are needed to enhance densification kinetics using smaller-sized particulates, applied pressure, and/or sintering additives.

CONTENTS

SUMMARY	iii
INTRODUCTION	1
ELECTROLYSIS TESTS: TITANIUM DIBORIDE-GRAPHITE REPLACEABLE CATHODE	2
IMMERSION TESTS IN MOLTEN ALUMINUM	11
HIGH-PURITY TITANIUM DIBORIDE: 140-HOUR TEST	14
REPLACEABLE ANODE-CATHODE FIXTURE	16
TITANIUM DIBORIDE-BASED PAINT COATING	20
IN SITU TITANIUM DIBORIDE COATING STUDY	23
TITANIUM DIBORIDE SINTERING STUDIES	26
CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH	27
ACKNOWLEDGMENTS	29
REFERENCES	31

FIGURES

1	Schematic of Small-Scale Cell Used to Evaluate TiB_2 -G Replaceable Cathodes	5
2	Schematic of Laboratory-Scale Cell Used to Evaluate TiB_2 -G Replaceable Cathodes	6
3	Microstructure of TiB_2 -G Cathode in Experiment 10-1-86.	6
4	Microstructure of TiB_2 -G Cathode in Experiment 9-9-86	7
5	Thickness of Al Penetration Layer in TiB_2 -G Cathodes as a Function of Electrolysis Time	7
6	Microstructure of TiB_2 -G Cathode in Experiment 6-10-87	8
7	Elemental Map of Polished Cross Section of TiB_2 -G Cathode in Experiment 1-12-87	10
8	Microstructure of TiB_2 -G Composite Before and After Exposure to Molten Al^2 for 2 wk	13
9	The 140-h Electrolysis Test of an Alcoa High-Purity TiB_2 Cathode	15
10	Replaceable Anode-Cathode Fixture	17
11	Cross Section of $\text{NiO-NiFe}_2\text{O}_4$ -17 wt% Cu Anode After 7 h of Electrolysis in the Replaceable Anode-Cathode Fixture	18
12	Polished Section of TiB_2 -G and BN Replaceable Anode-Cathode Fixture After Test	19
13	TiB_2 -Based Paint Coating on Graphite before Exposure to Molten Al	22
14	TiB_2 -Based Paint Coating on Graphite after Exposure to Molten Al	23
15	Degradation of Ti after Exposure to Al for 4 h at 950°C	24
16	Degradation of Ti after Exposure to Al with 10 mol% B for 4 h at 950°C	25

TABLES

1	Small-Scale Cell Tests with TiB_2 -G Replaceable Cathode Fixtures	3
2	Laboratory-Scale Cell Tests with TiB_2 -G Replaceable Cathode Fixtures	4

INTRODUCTION

The Inert Electrode Program is being conducted by the Pacific Northwest Laboratory (PNL)^(a) 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 three tasks with the following objectives:

- Inert Anode Development - to improve the energy efficiency of Hall-Heroult cells by development of inert anodes.
- Stable Cathode Studies - to develop methods for retrofitting Hall-Heroult cells with titanium diboride (TiB_2)-based cathode materials.
- Sensor Development - to devise sensors to control the chemistry of Hall-Heroult cells using stable anodes and cathodes.

Enhanced energy efficiency during the electrolytic production of Al is possible using Al-wetted, TiB_2 -based cathodes which enable reduced voltage drop across the electrolyte by reducing the anode-cathode spacing. Several previous attempts to develop practical cell designs have been unsuccessful because of chemical attack of TiB_2 -based cathode materials and poor methods of attaching these materials to the electrolysis cell.^(b) Practical solutions are being evaluated under the Inert Electrode Program at PNL. Research has primarily entailed short-duration, laboratory-scale experiments which have demonstrated feasible design candidates for scale-up and acceptable wear-resistance of anodes and cathodes. These data support ongoing research to design a pilot cell that will be used for evaluating the feasibility of retrofitting existing commercial plants with the inert electrode technology.

(a) Operated for DOE by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

(b) Published research pertaining to Al-wetted cathodes for the aluminum industry is reviewed by Billehaug and Oye (1980) and Schilling, Hagen, and Hart (1987).

This report summarizes the research activities of the Stable Cathode Studies task for FY 1987; an abbreviated summary is reported by Strachan et al. 1988 (draft).^(a) The main objective of the research has been to evaluate feasible approaches for retrofitting existing Hall-Heroult cells with TiB_2 -based cathodes. Analyses were intended to support retrofit concepts entailing use of inert anodes. Laboratory experiments were performed to analyze the wear behavior of TiB_2 -based cathodes used in prime candidate cell designs, which were selected based on a literature review (Schilling, Hagen, and Hart 1987) and previous research (Hart et al. 1987). Analyses primarily involved microstructure evaluation of TiB_2 -based materials before and after electrolysis with $NiO-NiFe_2O_4$ -based anodes.

The majority of the experiments were performed to evaluate replaceable cathodes, which rest, unattached, on carbonaceous cell bottoms. Preliminary experiments were also performed to evaluate 1) replaceable electrode fixtures having ceramic spacers to attach the anodes to the cathodes and align the anode-cathode spacing, 2) TiB_2 -based paint coatings, 3) in situ formation of TiB_2 coatings which may be self-healing in an operating Hall-Heroult cell, and 4) fabrication of TiB_2 cathodes by sintering TiB_2 powder that has been prepared by a low-temperature precursor process. In addition, the microstructure behavior of four types of TiB_2 -based materials was evaluated during nonpolarized immersion in Al.

ELECTROLYSIS TESTS: TITANIUM DIBORIDE-GRAPHITE REPLACEABLE CATHODE

Titanium diboride-graphite (TiB_2 -G) composites^(b) were evaluated as replaceable cathodes in electrolysis tests of up to 95 h duration using cermet anodes. Replaceable cathodes, originally proposed by Goodnow and Payne (1982), entail use of TiB_2 -based articles which rest, unattached, on carbonaceous cell bottoms. Replaceable cathodes are desired over TiB_2 -based

(a) Strachan, D. M. et al. Inert Electrode Program Fiscal Year 1987 Annual Report. Pacific Northwest Laboratory, Richland, Washington. Draft report to sponsor.

(b) TiB_2 -G type B composites were supplied by L. Joo of Great Lakes Research Corporation, Elizabethton, Tennessee.

articles which are rigidly attached to carbonaceous cell bottoms, because dimensional instabilities in the cell bottoms may cause fracture or detachment of TiB_2 -based articles. The TiB_2 -G composites exhibited acceptable performance in nearly all of the electrolysis tests with minimal indication of physical damage. However, one test showed TiB_2 fragments that were suspended in Al. The wear behavior of a TiB_2 -G cathode was evaluated using high-resolution optical ceramography and elemental mapping. Aluminum was found to replace the graphite contained within the TiB_2 pores at the surfaces of the sample. Beneath this layer, the TiB_2 pores exhibited a reaction layer concentrated with Na and F and depleted of Al and C. Chemical reactions occurring in this layer may possibly control the overall wear resistance and useful life of these materials.

A summary of the electrolysis test conditions is shown in Tables 1 and 2. In each of the small-scale cells, a TiB_2 -G plate was loosely set into a slotted cavity in the prebaked C cell bottom (Figure 1). In each of the laboratory-scale cells, a TiB_2 -G disc was set in place on the graphite cell bottom (Figure 2). All tests were started by heating the cell with a layer of Al on top of the TiB_2 -G; this procedure was used to prevent chemical attack of the TiB_2 -G caused by contact with cryolite (Na_3AlF_6) bath (Hart et al. 1987). In addition, all of the electrolysis tests were performed in

TABLE 1. Small-Scale Cell Tests with TiB_2 -G Replaceable Cathode Fixtures^(a)

Experiment Date	Electrolysis Duration, h	Anode-Cathode Spacing, cm	Anode Composition
10-1-86	95	3.8	NiD-NiFe ₂ O ₄ -17 wt% Cu
1-5-87	43.5	3.2	NiO-NiFe ₂ O ₄ -17 wt% Cu
1-12-87	24	1.9	NiO-NiFe ₂ O ₄ -17 wt% Cu
2-11-87	30	1.9	NiO-NiFe ₂ O ₄ -X ^(b)

(a) Each cell has a TiB_2 -G replaceable cathode that is shaped as a rectangular parallelepiped of 7.6 x 14.0 x 25.0 mm in size. Tests were operated between 1 A and 5 A with a bath composition of 79.6 wt% Na_3AlF_6 -13.5 wt% AlF_3 -8 wt% alumina (Al_2O_3) (bath ratio = 1.08). All tests were performed at 970°C.

(b) X refers to a proprietary composition.

TABLE 2. Laboratory-Scale Cell Tests with $\text{TiB}_2\text{-G}$
Replaceable Cathode Fixtures^(a)

Experiment Date	Anode-Cathode Spacing, cm	Anode Composition, wt%	Bath Composition, wt%
6-10-87 [44B]	7.7	$\text{NiO-NiFe}_2\text{O}_4$ - 17 wt% Cu	72.7 Na_3AlF_6 -11.6 Al_2O_3 -11.7 AlF_3 - 4 CaF_2 (1.07 Bath Ratio)
7-14-87 [49-3]	8.1	$\text{NiO-NiFe}_2\text{O}_4$ - 17 wt% Cu	67.1 Na_3AlF_6 -4.5 Al_2O_3 -13.4 AlF_3 - 10 CaF_2 -5 MgF_2 (1.0 Bath Ratio)
7-14-87 [50-8]	8.4	$\text{NiO-NiFe}_2\text{O}_4$ - 17 wt% Cu	73.3 Na_3AlF_6 -2 Al_2O_3 -14.7 AlF_3 - 10 CaF_2 (1.0 Bath Ratio)
7-20-87 [52]	7.1	$\text{NiO-NiFe}_2\text{O}_4$ - 17 wt% Cu	78.5 Na_3AlF_6 -8 Al_2O_3 -9.5 AlF_3 - 4 CaF_2 (1.15 Bath Ratio)
8-10-87 [54]	7.6	$\text{NiO-NiFe}_2\text{O}_4$ - 17 wt% Cu	78.5 Na_3AlF_6 -8 Al_2O_3 -9.5 AlF_3 - 4 CaF_2 (1.15 Bath Ratio)
8-20-87 [55]	9.8	$\text{NiO-NiFe}_2\text{O}_4$ - $\chi^{(b)}$	78.5 Na_3AlF_6 -8 Al_2O_3 -9.5 AlF_3 - 4 CaF_2 (1.15 Bath Ratio)
8-20-87 [56]	8.9	$\text{NiO-NiFe}_2\text{O}_4$ - 17 wt% Cu	78.5 Na_3AlF_6 -8 Al_2O_3 -9.5 AlF_3 - 4 CaF_2 (1.15 Bath Ratio)

(a) Electrolysis was performed for 20 h in all experiments, except 7-14-87 [49-3] which was 11.6 h. The $\text{TiB}_2\text{-G}$ disc size was 67 mm diameter x 9 mm thick for all experiments except for 8-20-87 [56], which used a larger disc, 94 mm diameter x 9 mm thick. All tests were operated at 970°C at 10 to 25 A.

(b) X refers to a proprietary composition.

conjunction with the anode evaluation task; therefore, anode-cathode spacings were made large enough to prevent anode degradation caused by contact with molten Al.

Optical ceramography revealed four key features typical of all $\text{TiB}_2\text{-G}$ cathodes evaluated in the small-scale cell (Figures 3 and 4): 1) wetting of the exterior surfaces by Al, 2) no evidence of Al contamination caused by fragmentation of the TiB_2 matrix, 3) an Al penetration layer filling the TiB_2 pores directly beneath the exterior surfaces of the $\text{TiB}_2\text{-G}$, and 4) a reaction layer in the TiB_2 pores directly beneath the Al penetration layer. The

FIGURE 1. Schematic of Small-Scale Cell Used to Evaluate TiB₂-G Replaceable Cathodes

nature of this reaction layer is described below using elemental mapping. The thicknesses of the Al penetration layers were measured from micrographs of the polished samples. Aluminum penetration (Figure 5) reached a maximum depth of 250 to 275 μm after 90 h of electrolysis.

The TiB₂-G discs were removed intact from the laboratory-scale cells with no visual evidence of physical damage; however, optical ceramography performed on sample 6-10-87 [44B] revealed TiB₂ fragments suspended in Al (Figure 6). The exact cause of the TiB₂ fragmentation was not positively established, although previous studies (Hart et al. 1987) suggest that Na₃AlF₆ bath attack may be responsible. The layer of bath instead of Al directly above the top surface of the TiB₂-G in Figure 6 may have resulted

FIGURE 2. Schematic of Laboratory-Scale Cell Used to Evaluate $\text{TiB}_2\text{-G}$ Replaceable Cathodes

FIGURE 3. Microstructure of $\text{TiB}_2\text{-G}$ Cathode in Experiment 10-1-86. The cracks existed in as-received samples and appear to have no affect on wear resistance.

FIGURE 4. Microstructure of TiB₂-G Cathode in Experiment 9-9-86. TiB₂ is the light-colored, interconnected phase; the material is produced with graphite inside the TiB₂ pores.

FIGURE 5. Thickness of Al Penetration Layer in TiB₂-G Cathodes as a Function of Electrolysis Time. The penetration depth increased with electrolysis time.

FIGURE 6. Microstructure of $\text{TiB}_2\text{-G}$ Cathode in Experiment 6-10-87 [44B]. The top surface (center and below) of the $\text{TiB}_2\text{-G}$ is coated with bath. The cracks are related to materials processing, as they also appear in the as-received samples.

from sedimentation of undissolved Al_2O_3 after electrolysis started. Manual stirring indicated that Al_2O_3 supersaturation occurred near the end of the test; the relative buoyancies of the phases present suggest that undissolved Al_2O_3 may have displaced the Al pad that was originally present above the TiB_2 -G when the cell was heated. The remaining tests in the laboratory-scale cells were performed without supersaturating the bath with Al_2O_3 ; the top surfaces of the TiB_2 -G cathodes appeared to be in direct contact with Al (and not Na_3AlF_6 bath), based on visual observations of the uncut samples dismantled from the cells. However, optical ceramography was not performed on these samples to confirm the absence of TiB_2 fragmentation.

The behavior of a TiB_2 -G cathode was further evaluated using optical ceramography and x-ray spectroscopy elemental mapping. Figure 7 shows results from a cross section of the anode-facing surface of a TiB_2 -G cathode that was electrolysis tested for 24 hours in the small-scale cell (experiment 1-12-87). The ceramography and elemental mapping indicate 1) no evidence of TiB_2 microcracking, fragmentation, or intergranular penetration by Al, 2) depletion of the graphite phase within the TiB_2 pores to a depth of 200 to 250 μm beneath the surface of the cathode, 3) a molten Al penetration layer that fills the TiB_2 pores up to a depth of 50 to 80 μm beneath the exterior surface of the cathode, 4) a Na- and F-rich layer depleted in C and Al directly beneath the molten Al penetration layer, and 5) the presence of Na and F throughout the TiB_2 pores in the remainder of the sample. Although the F map is not shown in Figure 7, the F map appeared nearly identical to the Na map. The observation of Na and F within TiB_2 pores in the bulk of the sample suggests the possibility of a polishing artifact, and/or that Na and F may have indeed migrated to the interior of the composite during electrolysis. Such migration is possible, considering Na intercalation through graphite and bath penetration through the open pores of the TiB_2 -G.(a)

The elemental map raises some important concerns regarding the basic chemical reactions affecting the wear resistance of these materials. Although these materials are reported to exhibit minimal deterioration in 6-mo electrolysis tests (Tucker et al. 1986; Tabereaux 1987), the properties

(a) TiB_2 -G exhibits 25 vol% porosity according to Tabereaux (1987).

FIGURE 7. Elemental Map of Polished Cross Section of TiB_2 -G Cathode in Experiment 1-12-87.
 A = Al Coating; B = Anode-Facing Edge; C = Reaction Zone; D = TiB_2 ; E = Graphite.

of the primary constituents (TiB_2 and graphite) suggest the possibility that surface reactions in the TiB_2 -G may be controlling cathode lifes. Specifically, it may be suggested that fragmentation of brittle TiB_2 is possible as a result of expansion stresses exerted on the TiB_2 pore walls. These expansion stresses can originate from volumetric expansion of graphite as a result of Na intercalation and salt crystallization^(a) and the volume expansion associated with the formation of Al_4C_3 from graphite.^(b) Chemical reactions and transport processes occurring in the Na-rich layer may also have life-limiting effects, as the structure of this layer may affect 1) the rate of Na intercalation into the graphite and consequently the graphite expansion rate beneath this layer, 2) the rate of Al_4C_3 formation and subsequent dissolution into the Al pad, and 3) the rate of bath penetration into the open porosity of the TiB_2 -G. Additional research with these materials is needed to evaluate chemical reactions and transport processes that are associated with the Na-rich layer and may be life-limiting. Additional data pertaining to reactions in this layer are shown below by comparing microstructural behavior of TiB_2 -G before and after nonpolarized exposure to Al.

IMMERSION TESTS IN MOLTEN ALUMINUM

The microstructural behavior of four types of TiB_2 -based materials was evaluated before and after immersion in molten Al. The samples were submerged in Al with no Na_3AlF_6 present at 970°C under an Ar atmosphere for various time durations of up to 20 wk. The test samples included Alcoa-supplied high-purity TiB_2 ^(c), PNL-fabricated TiB_2 -AlN composites, composites of chemical-vapor-infiltrated TiB_2 on ceramic fiber mesh^(d) and TiB_2 -G

-
- (a) Waddington 1963; Sorlie and Oye 1984a and 1984b; Panebianco and Bacchiega 1966; Dell 1967 and 1985; Dewing 1963 and Dewing 1974.
 - (b) Based on the $4\text{Al} + 3\text{C} = \text{Al}_4\text{C}_3$ reaction, 3.8 cm³ of Al_4C_3 is formed from 1 cm³ of graphite (Weast, Astle, and Beyer 1985; Schilling and Graff 1988).
 - (c) Samples were provided by R. Baumgartner of Alcoa Laboratories, Alcoa Center, Pennsylvania.
 - (d) Samples were provided by T. Besmann of Oak Ridge National Laboratory. The chemical vapor infiltration process is described by Caputo and Lackey (1984), Caputo, Lackey, and Stinton (1985), and Stinton et al. (1986). Samples contained Nicalon SiC-based fibers and produced by Nippon Carbon Co., Tokyo, Japan.

type B composites supplied by Great Lakes. Each sample was contained in an Al_2O_3 crucible; heating and cooling rates were approximately $3^\circ\text{C}/\text{min}$. Details of these studies are reported by Schilling and Graff (1988).

Key results from this study were that Alcoa-supplied high-purity TiB_2 and PNL-fabricated TiB_2 -AlN composites exhibited superior resistance to chemical attack, with no evidence of fragmentation or intergranular penetration by Al. Composites of chemical-vapor-infiltrated TiB_2 on ceramic fiber mesh exhibited mixed results. The TiB_2 coatings were resistant to chemical attack, but the SiC-based fibers reacted with molten Al during the first 4 wk of exposure. Additional research is needed to evaluate more wear-resistant fibers for these composites, as the processing of fiber mesh structures has two potential advantages over traditional powder sintering methods of processing TiB_2 -based monoliths: 1) a significantly greater variety of shapes can be processed and 2) smaller amounts of relatively high-cost TiB_2 (with thin-coated structures) are needed. Possible fiber candidates which are being developed by various ceramic manufacturers include AlN, BN, Al_2O_3 , and high-purity SiC.

Another key result from the immersion tests was that Great Lakes TiB_2 -G composites were extensively attacked within 8 h of exposure. Typical features included intergranular penetration of TiB_2 by Al and Al_4C_3 formation as a result of direct reaction between Al and graphite in the TiB_2 -G (Figure 8). Analyses by x-ray diffraction were performed on cut surfaces of an immersion test specimen, and the results suggest that the graphite is totally consumed by the formation of Al_4C_3 (Schilling and Graff 1988). Anoxic conditions during the immersion tests are not expected to result in a mechanism for rapid removal of Al_4C_3 from the TiB_2 pores; therefore, it may be suggested that stresses are exerted on the TiB_2 pore walls as a result of the 3.8:1 volume expansion of Al_4C_3 relative to graphite (Weast, Astle, and Beyer 1985; Schilling and Graff 1988). It is hypothesized that this process may fracture the brittle TiB_2 matrix, subsequently exposing Al to deeper regions of the composite and allowing the attack process to proceed inward from the exterior surfaces. Supporting this hypothesis, molar volume calculations and

Before:

2 mm

100 μ m

After:

FIGURE 8. Microstructure of TiB₂-G Composite Before and After Exposure to Molten Al for 2 wk. TiB₂ and graphite are the light- and dark-colored phases in the unexposed material.

solubility calculations suggest that, if all of the C present formed Al_4C_3 during the immersion tests, the saturation solubility of Al_4C_3 in Al would be exceeded by several times (Schilling and Graff 1988). As a result, dissolution rates would approach zero as the saturation solubility was reached, and Al_4C_3 crystals would accumulate without dissolving inside the TiB_2 pores.

This form of attack may never occur in a TiB_2 -G cathode, because the literature suggests that Hall cell conditions favor the rapid removal of Al_4C_3 from Al-graphite interfaces and into Al. It is possible that this process prevents disruption of the TiB_2 matrix during electrolysis, because of the rapid removal of Al_4C_3 from the Al-filled TiB_2 pores. In support of this argument, several authors report that Al in Hall cells typically contains Al_4C_3 at concentrations of 10 to 25 ppm, which are well below the saturation solubility of approximately 360 ppm at 960°C . As a result, Al_4C_3 formed at Al-graphite interfaces is expected to dissolve into the metal pad during electrolysis; the Al_4C_3 subsequently diffuses through the Al and Na_3AlF_6 bath and is removed from the cell by reacting with CO_2 or O_2 at the anode (Hollingshead and Brown 1981; Takemoto et al. 1963; Dorward 1973a and 1973b; Grjotheim, Naeumann, and Oye 1977). Transport of Al_4C_3 may be by a similar mechanism during electrolysis with cermet anodes. In addition, the existence of a Na-rich layer observed within the TiB_2 -G cathodes (Figure 7) may affect the rate of Al_4C_3 formation and subsequent dissolution into the Al pad.

HIGH-PURITY TITANIUM DIBORIDE: 140-HOUR TEST

Alcoa high-purity polycrystalline TiB_2 was evaluated as a replaceable cathode in a 140-h bench-scale electrolysis test. The TiB_2 exhibited acceptable performance with no evidence of microcracking or penetration by Al or Na_3AlF_6 bath, based on optical ceramography analysis.

The TiB_2 was supplied by R. Baumgartner of Alcoa Laboratories in the form of a tile that was sintered from high-purity powders produced by the halide plasma reduction process; this material is reported to exhibit superior resistance to chemical attack by molten Al (Hoejke 1981; Baumgartner and Steiger 1984; Baumgartner 1984a and 1984b). The as-received TiB_2 was cut

FIGURE 9. The 140-h Electrolysis Test of an Alcoa High-Purity TiB_2 Cathode. Schematic of cell is shown on the right. The TiB_2 shows no evidence of microcracking, spalling, or penetration by Al or Na_3AlF_6 bath.

into a rectangular parallelepiped (32 x 20 x 6.6 mm) for electrolysis testing in the small-scale cell (Figure 9); this design is similar to that reported by Foster and Jacobs (1978). Electrolysis was performed at 970°C with a bath composition of 79.6 wt% Na_3AlF_6 -13.5 wt% AlF_3 -8 wt% Al_2O_3 (bath ratio = 1.08). The cermet anode was made of $\text{NiO-NiFe}_2\text{O}_4$ -X.^(a) The TiB_2 tile fell

(a) X refers to a proprietary composition.

out of its retaining slot as a result of manual probing during the test. Electrolysis was terminated after 140 h when it was discovered that the Na_3AlF_6 bath had successively penetrated through the Al_2O_3 , graphite, and Inconel® walls of the cell; this penetration was observed at the level of the bath/air interface.

As indicated in Figure 9, optical ceramography showed no evidence of microcracking, spalling of TiB_2 grains, or any apparent penetration by Na_3AlF_6 or Al. A layer of Al was observed coating portions of the exterior surfaces of the tile. This film contained a second phase that possibly resulted from Fe contamination after the Fe-based sidewall of the cell was penetrated by Na_3AlF_6 bath during electrolysis. Further analysis was not performed to identify this phase nor were attempts made to analyze the TiB_2 at higher magnification.

REPLACEABLE ANODE-CATHODE FIXTURE

A small-scale electrolysis test of a replaceable anode-cathode fixture (Figure 10) was performed, using a BN spacer to mechanically align anode-cathode spacing. This design concept, originally proposed by Jarrett and Hornack (1985), was evaluated because it has unique advantages: 1) anodes and cathodes are contained in removable fixtures, which may be easily retrofitted to existing commercial cells, 2) anode-cathode spacings are precisely fixed because the anode and cathode surfaces are separated by ceramic spacers and the cathodes do not physically contact cell bottoms which are dimensionally unstable, and 3) the replaceable fixtures can accommodate bipolar electrodes, which are revolutionary design candidates for advanced energy-saving cells.

The replaceable cathode fixture was constructed using a TiB_2 -G cathode, a $\text{NiO-NiFe}_2\text{O}_4$ -17 wt% Cu anode brazed to a Ni rod current lead, and a BN sleeve attached to both electrodes and fixing the anode-cathode spacing at 1.3 cm. The TiB_2 -G cathode was composed of an assembly of two machined

® Inconel is a trademark of Huntington Alloys (INCO Alloys International) Huntington, West Virginia.

FIGURE 10. Replaceable Anode-Cathode Fixture. The fixture was evaluated in a 7-h electrolysis test in a small-scale cell. A cut section of the fixture is shown on the right.

pieces: a cylindrical shaft containing a flange at one end which was loosely fitted inside the center of a larger-diameter collar. Electrolysis was performed at 970°C in the small-scale cell using a bath composition of 79.6 wt% Na_3AlF_6 -13.5 wt% AlF_3 -8 wt% Al_2O_3 (bath ratio = 1.08). Current densities for the anode and cathode were approximately 1 A/cm^2 . The cell operated for 7 h with a total voltage drop of 3.4 volts. The assembled fixture was subsequently sectioned with a diamond saw and polished for optical ceramography.

The anode exhibited evidence of minimal wear (Figure 11). The BN and $\text{TiB}_2\text{-G}$ remained intact, but both materials showed features of surface attack (Figure 12). The BN lost approximately 1 mm of material at regions directly facing the anode-cathode spacing. More wear-resistant spacer materials need to be evaluated, such as AlN or a $\text{NiO-NiFe}_2\text{O}_4$ -based material used to make the matrix phase of the cermet anodes.

Optical ceramography (Figure 12) indicated a thin layer of Al coating the exterior surfaces of the $\text{TiB}_2\text{-G}$; surface attack was also visible in the

FIGURE 11. Cross Section of $\text{NiO-NiFe}_2\text{O}_4$ -17 wt% Cu Anode After 7 h of Electrolysis in the Replaceable Anode-Cathode Fixture. Minimal degradation of the anode and braze joint is observed.

form of microcracks in the TiB_2 . Cracks in the TiB_2 matrix appeared directly beneath the exterior surfaces of the TiB_2 -G and running parallel to these surfaces. For example, cracks extended the full width of the cathode directly beneath the interpolar spacing (Figure 12). Similar features were frequently observed beneath the remaining surfaces of the TiB_2 -G. The cracks predominantly ran along an interface between what appeared to be the unreacted graphite in the interior of the TiB_2 -G and a reaction layer that was visible within the TiB_2 pores at the exterior surfaces of the TiB_2 -G.

FIGURE 12. Polished Section of TiB₂-G and BN Replaceable Anode-Cathode Fixture After Test

The TiB_2 -G also exhibited surface attack in the form of spalled TiB_2 grains that were entrained in the Al or Na_3AlF_6 bath (Figure 12). Spalling of TiB_2 grains was most frequently evident at portions of the cathode that protruded into the Al pad during electrolysis. Based on previous experiments, the fragmentation of the TiB_2 may have been caused by the chemical attack by the Na_3AlF_6 bath; this phenomenon may be avoided if the TiB_2 -G is coated with a protective layer of Al prior to exposure to molten Na_3AlF_6 (Hart et al. 1987).

The cell operated at approximately 50% current efficiency, based on the weighed amount of Al produced during electrolysis. It is possible that the low efficiency is caused by gas bubble resistance at the anode. Minimized bubble resistance, through improved circulation of electrolyte, is necessary for large-scale fixtures operating at anode-cathode spacings of less than 1 to 2 cm. Improved mechanical designs need to be evaluated, such as those using grooves in the bottom surfaces of the anode to carry the gas bubbles away from the anode-cathode spacing.

TITANIUM DIBORIDE-BASED PAINT COATING

The performance of an Aremco^(a) TiB_2 -based paint coating on graphite was evaluated during short-term exposure to molten Al under nonpolarized conditions. Paint coatings were evaluated because they provide a relatively inexpensive approach to producing elaborate shapes with a thin coating of TiB_2 -based material. The coatings that were soaked in molten Al were extensively attacked. This attack may result from molten Al penetration through pre-existing cracks in the coating, causing chemical attack of the graphite and reactions between the Al and SiO_2 , a primary constituent of the coating. We recommend that future research focus on developing coatings that are less susceptible to cracking and developing coating formulations that are less reactive to molten Al.

(a) Aremco Products, Inc., Ossining, New York, Graphi-Coat 623.

A sample of graphite^(a) was cut into a small cube (approximately 1 cm on each side), and all sides were subsequently brush-coated with a TiB₂-based paint. The coating was dried and heat treated according to manufacturer instructions. The sample was soak tested in molten Al with no Na₃AlF₆ present at 970°C for 4 wk under a flowing Ar atmosphere, then sectioned and polished for optical ceramography. No further experimental analysis was performed.

As indicated in Figures 13 and 14, the paint coating was penetrated by Al, and the graphite was extensively deteriorated. Figure 13 indicates cracks in the coating prior to the soak test in molten Al. It is possible that molten Al penetrated these cracks, leading to contact with the graphite and the subsequent formation of Al₄C₃. The formation of Al₄C₃ from elemental Al and C is thermodynamically favored at 970°C; -35.1 kcal is the standard Gibbs free energy for the formation of one mole of Al₄C₃ at 970°C (Kubaschewski and Alcock 1979). In addition, the 3.8:1 volume expansion of Al₄C₃, relative to graphite, may have contributed to the disruption of the coating leading to further penetration by Al (Schilling and Graff 1988; Weast, Astle, and Beyer 1985).

Another cause for the attack may be the chemical reactions between molten Al and SiO₂, which is a major constituent of the coating according to the manufacturer. The reduction of SiO₂ to form Al₂O₃ and Si metal at temperatures as low as 700°C has been reported elsewhere (Brondyke 1953; Standage and Gani 1967). Free energy calculations also suggest the possibility of this reaction (Kubaschewski and Alcock 1979):

Reaction	Standard Gibbs' Free Energy at 970°C, kcal
$3\text{SiO}_2 = 3\text{Si} + 3\text{O}_2$	+492.1
$4\text{Al} + 3\text{O}_2 = 2\text{Al}_2\text{O}_3$	-611.2
$4\text{Al} + 3\text{SiO}_2 = 2\text{Al}_2\text{O}_3 + 3\text{Si}$	-119.1

(a) Poco Graphite, Inc., Decatur, Texas; Research grade graphite type PPE-109.

FIGURE 13. TiB_2 -Based Paint Coating on Graphite Before Exposure to Molten Al

FIGURE 14. TiB_2 -Based Paint Coating on Graphite After Exposure to Molten Al.² Large fragments of the coating are visible at the bottom of the crucible and no pieces of unreacted graphite are evident.

IN SITU TITANIUM DIBORIDE COATING STUDY

Preliminary experiments were performed to evaluate in situ formation of TiB_2 coatings that may be self-healing in a Hall-Heroult cell. Synthesis of TiB_2 coatings was attempted by soaking Ti in B-saturated molten Al. Aluminum-titanium reactions resulted in extensive degradation of Ti. Although this preliminary test was unsuccessful, further evaluation is recommended, as there are significant economic advantages to self-healing TiB_2 cathodes in a Hall cell. A larger development program is needed to evaluate the feasibility of alternative coating methods, such as electrodeposition and diffusion saturation using molten salts.^(a)

During the experiments, Ti rods (3.2 cm diameter x 2.5 cm high) were exposed to either molten Al or Al-10 mol% B for 4 h at 950°C in Al_2O_3 crucibles under a flowing Ar atmosphere. The 10% B solution was prepared by

(a) Sane, Wheeler, and Kuivila 1983 and 1985; Singhal 1978; and Epik 1977; Samsonov and Epik 1966.

mixing weighed amounts of Al and B powder into an Al_2O_3 crucible. The crucibles were cross sectioned with a diamond saw after the test; optical ceramography showed extensive attack at the outer surfaces of the Ti rods in both tests (Figures 15 and 16). Microchemical analysis of reaction products was not performed, although the Al-Ti phase diagram suggests the formation of

FIGURE 15. Degradation of Ti after Exposure to Al for 4 h at 950°C. Reaction zones appear at the outer surfaces of the Ti

FIGURE 16. Degradation of Ti after Exposure to Al with 10 mol% B for 4 h at 950°C. Reaction zones appear at the outer surfaces of the Ti.

phase separation from Al-Ti compound formations. The TiB_2 is also expected to be present in the reaction layer around the sample that was exposed to the 10% B solution, based on the negative Gibbs free energy of the $\text{Ti} + 2\text{B} > \text{TiB}_2$ reaction (Zavitsanos and Morris 1983).

TITANIUM DIBORIDE SINTERING STUDIES

A brief set of experiments was performed to evaluate the feasibility of sintering TiB_2 from powders prepared by a novel process involving the low-temperature synthesis of a TiB_2 precursor (Ritter 1987). The powder was supplied by J. Ritter, the inventor of the process, at the National Bureau of Standards. The ultimate goal of this study was to prepare cathodes for electrolysis testing. Unfortunately, cathode test samples could not be produced because of insufficient densification during sintering. However, processing modifications may be used to improve sinterability. With improved sinterability, these powders may have economic advantages over traditional powder processing and sintering methods, if fabrication costs are reduced and acceptable wear resistance is shown in a Hall cell. A larger development program is needed to evaluate these and other types of TiB_2 powders as they become available.

Experimental procedures were as follows. The as-received powder was examined with scanning electron microscopy, and particles were measured at 10 to 100 μm in size. Dry powders were mixed with a small amount of Carbowax® and mechanically pressed into a pellet before pressureless sintering at 1800°C for 4 h under a flowing Ar atmosphere. The pellet was not well sintered, as powder could be removed by abrading the surface of the pellet with a knife blade. Sintering temperatures of 2000°C and 2200°C did not significantly improve the densification of the powder.

Based on these observations, it is concluded that enhanced densification must be achieved before studies can be performed to evaluate the wear behavior of these materials in a Hall cell. It may be possible to enhance densification kinetics using smaller average particle sizes, higher sintering temperatures, and/or applied pressure such as with hot pressing methods. Impurity levels were not evaluated for these powders; therefore, it is uncertain to what extent impurities may have affected densification kinetics.

© Trademark of Doak Pharmacal Co., Inc., Westbury, New York.

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

Based on research to date, two approaches are recommended for achieving a practical, near-term retrofit of existing Hall-Heroult cells using drained cathodes, cermet anodes, and reduced anode-cathode spacing: 1) use of replaceable cathodes that rest, unattached, on C cell bottoms, and 2) use of replaceable anode-cathode fixtures that have ceramic spacers to align anode-cathode spacing. Both of these options require wear-resistant cathode materials; TiB_2 -G, TiB_2 -AlN, and high-purity TiB_2 are three prime candidates for both design approaches.

The replaceable cathode is the more conservative approach, as minimal alterations to the structure and operation of existing Hall-Heroult cells are possible, and the TiB_2 -based parts may be retrieved and serviced without cell shutdown or major reconstruction. However, a long-term drawback to the replaceable cathode approach is that the anode-cathode spacings may become misaligned as a result of dimensional instabilities in the cell bottom caused by Na intercalation and salt crystallization. Anode-cathode spacings, for cermet anodes and drained TiB_2 -based cathodes with reduced anode cathode spacing, must be precisely aligned to improve power efficiency and reduce electrode wear.

The replaceable anode-cathode fixture appears to overcome the misalignment problem; however, the main difficulty is that wear-resistant spacer materials must be evaluated. If wear-resistant spacer materials are established, breakthroughs in monopolar- and bipolar electrode designs could be possible that would require minimum alteration to existing Hall-Heroult cells. Prime candidate spacer materials for evaluation include AlN and possibly a NiFe_2O_4 -based phase similar to the cermet anode matrix.

To reach the long-range objective of retrofitting commercial cells with drained TiB_2 -based cathodes, cermet anodes, and reduced anode-cathode spacing, it is recommended that near-term research objectives focus on developing a basis for designing a 5- to 10-kA pilot cell. Replaceable TiB_2 -G cathodes, such as those being developed by Reynolds Corporation and Great Lakes Research Corporation (Tucker et al. 1986; Tabereaux 1987), are recommended for conservative cell designs that will enable near-term evaluation of

electrode wear behavior and expected energy efficiency for largescale cells. It is recommended that research activities be pursued in two areas:

1) assembling a team of experts to evaluate design parameters pertaining to heat balance, cell magnetohydrodynamics, cell operations and related control systems, electrode wear processes, and the physical geometries of electrodes and electrode attachments, and 2) performing laboratory-scale electrolysis tests in support of the pilot cell design. The latter experiments are mainly for evaluation of anode-cathode geometries, electrode holder systems, gas bubble release, and electrode wear processes at reduced anode-cathode spacing.

In addition, new alternatives for processing TiB_2 -based cathode materials need to be evaluated. Traditionally, TiB_2 -AlN cathodes have been fabricated into simple shapes using costly hot pressing procedures. Other fabrication methods such as injection moulding or slip casting should be evaluated for producing acceptably dense parts with reduced costs and more complex shapes. Methods for fabricating TiB_2 -AlN cathodes with improved mechanical properties and thermal shock resistance are also needed.

Processing techniques leading to improved wear resistance of TiB_2 thin coatings also should be evaluated in light of advanced cell designs that conserve TiB_2 . For example, paint coatings and ceramic fiber-weave structures coated with TiB_2 by methods such as chemical vapor infiltration allow cell designs having complex cathode shapes that could not be achieved using traditional powder sintering techniques. Paint coatings could be developed using inexpensive TiB_2 powder suspended in a ceramic-based phase that is resistant to damage from mechanical stresses and chemical attack. Recommended avenues for developing fiber weave structures include analyses of more wear-resistant fibers. Although SiC-based fibers deteriorated in the immersion experiments discussed above in this report, fiber weave approaches should not be abandoned because alternative fiber materials, such as high-purity SiC, AlN, and Al_2O_3 may exhibit resistance to chemical attack. Research is also needed to evaluate in situ formation of TiB_2 coatings that may be self-healing in a Hall-Heroult cell. As mentioned earlier, recommended avenues of research would include analyses of available methods such as electrodeposition and diffusion saturation.

ACKNOWLEDGMENTS

Technical support by S. C. Marschman, P. E. Hart, D. M. Strachan, C. F. Windisch, N. T. Saenz, G. L. Graff, D. E. Smith, N. C. Davis, H. E. Kjarmo, H. E. Kissinger, W. Haupin, R. Keller, N. Jarrett, N. Richards, and L. Joo is gratefully appreciated. The author wishes to thank T. L. Gilbride and G. A. Downard for preparation of the manuscript.

REFERENCES

- Baumgartner, H. R. 1984a. "Mechanical Properties of Densely Sintered High-Purity Titanium Diborides in Molten Aluminum Environments," J. Amer. Ceram. Soc. Vol. 67, No. 7, pp. 490-497.
- Baumgartner, H. R. 1984b. "Subcritical Crack Velocities in Titanium Diboride Under Simulated Hall-Heroult Cell Conditions," Amer. Ceram. Soc. Bull. Vol. 63, p. 1172.
- Baumgartner, H. R., and R. A. Steiger. 1984. "Sintering and Properties of Titanium Diboride Made From Powder Synthesized in a Plasma-Arc Heater," J. Amer. Ceram. Soc. Vol. 67, No. 3, pp. 207-212.
- Billehaug, K., and H. A. Oye. 1980. "Inert Cathodes for Aluminum Electrolysis in Hall-Heroult Cells (I)." Aluminium 56:642.
- Brondyke, K. J. 1953. "Effect of Molten Aluminum on Alumina-Silica Refractories," J. Amer. Ceram. Soc., Vol. 36, No. 5, pp. 171-174.
- Caputo, A. J., and W. J. Lackey. 1984. "Fabrication of Fiber-Reinforced Ceramic Composites by Chemical Vapor Infiltration," Ceramic Engineering and Science Proceeding, 5(7&8):654-667 American Ceramics Society, Columbus, Ohio.
- Caputo, A. J., W. J. Lackey, and D. P. Stinton. 1985. "Development of a New Faster Process for the Fabrication of Ceramic Fiber Reinforced Ceramic Composites by Chemical Vapor Infiltration," Ceram. Eng. Sci. Proc. 6(7-8):694-706, Amer. Ceramic Society, Columbus, Ohio.
- Dell, M. B. 1967. "Potlining Failures in Aluminum Electrolysis Cells," J. Metals, March 1967, #pp. 14-17.
- Dell, M. B. 1985. "Potlining Failure Modes," Light Metals 1985, H. D. Bohner, editor, American Institute of Mining and Metallurgical Engineers, New York, pp. 957-966.
- Dewing, E. W. 1963. "The Reaction of Sodium with Nongraphitic Carbon: Reactions Occurring in the Linings of Aluminum Reduction Cells," Transactions of the Metallurgical Society of AIME, Vol. 227, December 1963, pp. 1328-1334.
- Dewing, E. W. 1974. "The Chemistry of the Alumina Reduction Cell," Can. Met. Quart., Vol. 13, pp. 607-618.
- Dorward, R. C. 1973a. "Aluminum Carbide Formation and Removal During Electrolytic Reduction and Hot Metal Processing Operations," Light Metals 1973, American Institute of Mining and Metallurgical Engineers, New York, pp. 105-118.

- Dorward, R. C. 1973b. "Aluminum Carbide Contamination of Molten Aluminum," Aluminium, Vol. 49, pp. 686-688.
- Epik, A. P. 1977. "Boride Coatings," in Boron and Refractory Borides, ed. V. I. Matkovich, Springer-Verlag. pp. 597-612.
- Foster, P. A., Jr., and S. C. Jacobs. 1978. "Electrolytic Production of Metal," U.S. Patent 4,071,420.
- Goodnow, W. H., and J. R. Payne. 1982. "Aluminum Reduction Cell Electrode." U. S. Patent 4,349,427.
- Grjotheim, K., R. Naeumann, and H. A. Oye. 1977. "Formation of Aluminum Carbide in the Presence of Cryolite Melts," Light Metals 1977, American Institute of Mining and Metallurgical Engineers, New York, pp. 233-242.
- Hart, P. E., B. B. Brenden, N. C. Davis, O. H. Koski, S. C. Marschman, K. H. Pool, C. H. Schilling, C. F. Windisch, and B. J. Wrona. 1987. Inert Anode/Cathode Program Fiscal Year 1986 Annual Report. PNL-6247, Pacific Northwest Laboratory Report, Richland, Washington.
- Hoejke, H. H. 1981. "Submicron Titanium Boride Powder and Method for Preparing Same," U.S. Patent 4,282,195.
- Hollingshead, E. A., and J. A. Brown. 1981. "Rate of Solution of Carbon in Molten Aluminum Under a Cryolite Melt," Light Metals 1981, American Institute of Mining and Metallurgical Engineers, New York, pp. 625-634.
- Jarrett, N., and T. R. Hornack. 1985. "Support Member and Electrolytic Method." U.S. Patent 4,504,366.
- Kubaschewski, O., and C. B. Alcock. 1979. Metallurgical Thermochemistry, Fifth Edition, Pergamon Press, New York.
- Panebianco, B., and R. Sacchiega. 1966. "Deformation Phenomena in the Bottoms of Electrolytic Reduction Cells for Production of Aluminum," Alluminio, 35(3), pp. 69-78.
- Ritter, J. J. 1987. "A Low-Temperature Chemical Process for Precursors to Boride and Carbide Ceramic Powders," Advances in Ceramics Volume 21: Ceramic Powder Science eds. G. L. Messing, K. S. Mazdidasni, J. W. McCauley, and R. A. Haber, American Ceramic Society Inc., Westerville, Ohio, pp. 21-31.
- Samsonov, G. V., and A. P. Epik. 1966. "Part 1. Coatings of High-Temperature Materials: Boride Coatings," Coatings of High Temperature Materials, ed. H. H. Hausner, Plenum Press, New York, pp. 7-34.
- Sane, A. Y., D. J. Wheeler, and C. S. Kuivila. 1983. "Aluminum Wettable Materials," European Patent Application EP 94353 A2.

- Sane, A. Y., D. J. Wheeler, and C. S. Kuivila. 1985. "Aluminum Wettable Materials for Aluminum Production," U.S. Patent 4,560,448.
- Schilling, C. H., D. I. Hagen, and P. E. Hart. 1987. "Stable Attachment of TiB_2 -Based Cathodes for the Aluminum Industry: Review and Recommendation," Pacific Northwest Laboratory Report PNL-6144.
- Schilling, C. H. and G. L. Graff. 1988. Immersion Tests of TiB_2 -Based Materials for Aluminum Processing Applications. PNL-6593, Pacific Northwest Laboratory, Richland, Washington.
- Singhal, S. C. 1978. "An Erosion Resistant Coating for Titanium and Its Alloys," Thin Solid Films 53(3):375.
- Sorlie, M., and H. A. Oye. 1984a. "Chemical Resistance of Cathode Carbon Materials During Electrolysis," Light Metals 1984, American Institute of Mining and Metallurgical Engineers, New York, pp. 1059-1071.
- Sorlie, M. and H. A. Oye. 1984b. "Deterioration of Carbon Linings in Aluminum Reduction Cells, Part II - Chemical and Physical Characterization of Cathode Carbons," Metallwissenschaft und Technik, 38, pp. 109-115.
- Standage, A. E., and M. S. Gani. 1967. "Reaction Between Vitreous Silica and Molten Aluminum," J. Amer. Ceram. Soc., Vol. 50, No. 2, pp. 101-105.
- Stinton, D. P., A. J. Caputo, R. A. Lowden, and T. M. Besmann. 1986. "Improved Fiber - Reinforced SiC Composites Fabricated by Chemical Vapor Infiltration," Ceramic Engineering and Science Proceedings, July - August 1986, American Ceramic Society, Columbus, Ohio, pp. 983-989.
- Tabereaux, A. T. 1987. "Stable TiB_2 -Graphite Cathodes for Aluminum Production," Cathode Workshop Proceedings, Light Metals Production Research Group, February 27-28, 1987, Carnegie-Mellon University.
- Takemoto, M., T. Yashimoto, K. Oida, and L. Yanagida. 1963. "Effect of Holding on Some Properties of Metal Tapped from Electrolytic Cells," in Extractive Metallurgy of Aluminum, Volume 2, Aluminum, ed., G. Gerard, Interscience, New York, pp. 435-452.
- Tucker, K. W., J. R. Shaner, J. T. Gee, and L. A. Joo. 1986. " TiB_2 -Graphite Cathodes in Aluminum Reduction Cells," Extended Abstracts Electrochemical Society Fall 1986 Meeting, San Diego, California.
- Waddington, J. 1963. "Processes Occurring in the Carbon Lining of an Aluminum Reduction Cell," Extractive Metallurgy of Aluminum, Volume 2, ed., G. Gerard, Wiley Interscience, New York, pp. 435-452.
- Weast, R. C., Astle, M. J., and Beyer, W. H. 1985. CRC Handbook of Chemistry and Physics Sixty-Sixth Edition, CRC Press, Boca Raton, Florida, p. B-68, p. B-84.

Zavitsanos, P., and J. R. Morris, Jr. 1983. "Synthesis of Titanium Diboride by a Self-Propagating Reaction," In Ceramic Engineering and Science Proceedings, Amer. Ceramic Society, Vol. 4 No. 7-8.

DISTRIBUTION

No. of
Copies

No. of
Copies

OFFSITE

M. J. McMonigle
U.S. Department of Energy
Office of Industrial Programs
Forrestal Building
Washington, DC 20585

T. J. Gross
U.S. Department of Energy
Office of Industrial Programs
Forrestal Building
Washington, DC 20585

R. L. Sheneman
U.S. Department of Energy
Office of Industrial Program
Forrestal Building
Washington, DC 20585

10 DOE Office of Scientific and
Technical Information

M. Adkins
National Southwire Aluminum
Company
P.O. Box 500
Hawesville, KY 42348

J. V. Anderson
WCVE3
EG&G Idaho, Inc.
Idaho Falls, ID 83415

D. Auburg
Bonneville Power Administration
P.O. Box 3621, PDX 97208
Portland, OR 97208

F. W. Baker
Ceramics Division
Alcoa Laboratories
Alcoa Center, PA 15069

M. Baltzell
Eastalco Aluminum Company
Alumax, Inc.
5601 Manor Woods
Frederick, MD 21701

J. A. Barclay
U.S. Bureau of Mines
2401 "E" Street N.W.
Washington, DC 20241

W. L. Barham
Kaiser Aluminum and Chemical
Corp.
P.O. Box 877
Pleasanton, CA 94566

H. Robert Baumgartner
Ceramics Division
Alcoa Laboratories
Alcoa Center, PA 15069

T. R. Beck
Electrochemical Technology
Corp.
1601 Dexter Avenue
Seattle, WA 98109

S. Berwagan
Bonneville Power Administration
P.O. Box 3621 K
Portland, OR 97208

T. M. Besmann
Metals and Ceramics Division
Oak Ridge National Laboratory
P.O. Box X, Bldg. 4515
Oak Ridge, TN 37831-6063

K. A. Blakely, President
Advanced Refractory
Technologies, Inc.
699 Hertel Ave.
Buffalo, NY 14207

No. of
Copies

M. H. Blenk
Du Pont
P.O. Box 787
Niagara Falls, NY 14302

L. G. Boxall
Martin Marietta Laboratories
1450 South Rolling
Baltimore, MD 21227

J. Bracher
Kaiser Aluminum and Chemical
Corp.
825 N.E. Multnomah St.,
Suite 960
Portland, OR 97232-2150

R. Bradt
Department of Materials Science
and Engineering
University of Washington FB-10
Seattle, WA 98195

J. J. Brown, Jr.
Materials Engineering
Virginia Polytechnic Institute
Blacksburg, VA 24061

A. Budner
Bonneville Power Administration
P.O. Box 3621--EPC
Portland, OR 97208

A. J. Caputo
Metals and Ceramics Division
Oak Ridge National Laboratory
P.O. Box X
Oak Ridge, TN 37831-6063

N. Clark
Bonneville Power Administration-
Industrial Conservation
P.O. Box 3621
Portland, OR 97208

No. of
Copies

A. Cooke
Martin Marietta Laboratories
1450 South Rolling
Baltimore, MD 21227

J. A. Coppola
Standard Oil Engineered
Materials Company
P.O. Box 156
Niagara Falls, NY 14302

R. Curtis
Materials Development
Corporation
81 Hicks Avenue
Medford, MA 02155

J. V. Day
Mail Drop 2232
Kaiser Aluminum and Chemical
Corp.
300 Lakeside Drive
Oakland, CA 94643

R. Dethlefsen
Maxwell Laboratories
8888 Balboa Ave.
San Diego, CA 92123

D. H. DeYoung
Alcoa Technical Center
Alcoa Center, PA 15069

S. Diamond
Battelle Columbus Laboratories
505 King Avenue
Columbus, OH 43201-2693

C. W. Doerr
The Stackpole Corporation
Cermag Division
201 Stackpole Street
St. Marys, PA 15857

No. of
Copies

R. C. Dorward
Kaiser Aluminum and Chemical
Corp.
P.O. Box 877
Pleasanton, CA 94566

G. L. Eitel
Stone & Webster Engineering
Corp.
Greenwood Plaza
P.O. Box 5406
Denver, CO 80217

R. Engdahl
Deposits and Composites, Inc.
318 Victory Drive
Herndon, VA 22070

J. F. Elliott
MIT
Room 4-138
77 Massachusetts Avenue
Cambridge, MA 02139

B. G. Epstein
A. D. Little, Inc.
600 Maryland Ave., S.W.
Washington, DC 20024

J. W. Evans
University of California
Dept. of Matl. Sci. and Mineral
Eng.
Berkeley, CA 94720

R. A. Fenimore
ICI Advanced Materials
Rollins Building, Eighth Floor
Wilmington, DE 19897

D. A. Figgins
ARCO Petroleum Products Co.
P.O. Box 61004
Anaheim, CA 92803-6104

No. of
Copies

T. Foley
Northwest Power Planning
Council
850 S.W. Broadway, Suite 1100
Portland, OR 97205

P. Foster
Alcoa Laboratories
P.O. Box 772
New Kensington, PA 15068

J. Gee
Great Lakes Research Corp.
P.O. Box 1031
Elizabethton, TN 37643

T. Gilligan
Eltech Systems Corp.
625 East Street
Fairport Harbor, OH 44077

W. M. Goldberger
Superior Graphite Co.
120 S. Riverside Plaza
Chicago, IL 60606

J. Goodwell
Center for Metals Production
Mellon Institute
4400 Fifth Avenue
Pittsburgh, PA 15213

J.A.S. Green
Martin Marietta Laboratories
1450 South Rolling
Baltimore, MD 21227

C. Griffin
Ceramatec Inc.
2425 S. 900 West
Salt Lake City, UT 84119

L. I. Grindstaff
Great Lakes Research Corp.
P.O. Box 1031
Elizabethton, TN 37643

No. of
Copies

J. Haggerty
MIT
Building 12, Room 009
77 Massachusetts Avenue
Cambridge, MA 02139

I. L. Harry
Electric Power Research
Institute
P.O. Box 10412
Palo Alto, CA 94303

W. Haupin
2820 7th Street Road
Lower Burrell, PA 15068

H. W. Hayden, Jr.
1419 East 21st Street
The Dalles, OR 97058

R. Hill
Union Carbide Corp.
P.O. Box 94637
Cleveland, OH 44101

H. F. Hillegass
Alcoa Wenatchee Works
P.O. Box 221
Wenatchee, WA 98807

D. G. Howitt
College of Engineering
University of California, Davis
Davis, CA 95616

G. R. Hyde
U.S. Bureau of Mines
2401 "E" Street N.W.
Washington, DC 20241

S. C. Jacobs
Primary Processing
Aluminum Company of America
Alcoa Technical Center
Alcoa Center, PA 15069

No. of
Copies

R. A. James
Kaiser Aluminum and Chemical
Corp.
E2111 Hawthorne Road
Mead, WA 99021

S. H. Jan
Tennessee Valley Authority
1850 Commerce Union Bank Bldg.
Chattanooga, TN 37401

N. Jarrett
149 Jefferson Avenue
New Kensington, PA 15068

J. Joesowicz
Material Development Laboratory
Atlantic Richfield
20717 Prairie Street
Chatsworth, CA 91311

A. R. Johnson
Kaiser Aluminum
P.O. Box 877
Pleasanton, CA 94366

J. Johnson
Intalco Aluminum Company
P.O. Box 937
Ferndale, WA 98248

M. H. Johnson
Alcoa Wenatchee Works
P.O. Box 221
Wenatchee, WA 98801

L. Joo
Great Lakes Research Corp.
P.O. Box 1031
Elizabethon, TN 37643

M. Karmous
Oregon State Department of
Energy
625 Marion Street, N.E.
Salem, OR 97310

No. of
Copies

R. Keller
RD 3
Roundtop Road
Export, PA 15632

C. Anderson
Columbia Aluminum Co.
85 John Day Dam Road
Goldendale, WA 98620

K. Krupinski
Mail Stop 57
U.S. Steel Technical Center
1 Technical Center Drive
Monroeville, PA 15146

G. Y. Lai
Cabot Corporation
P.O. Box 9013
Kokomo, IN 46902-9013

J. E. Lane
Ceramic Research and
Development Center
Westinghouse Electric
Corporation
1310 Beulah Road
Pittsburgh, PA 15235

Sai-Kwing Lau
Standard Oil Engineered
Materials Company
Niagara Falls R&D Center
P.O. Box 832
Niagara Falls, NY 14302

J. J. Leddy
Dow Chemical U.S.A.
1776 Building
Midland, MI 48640

W. W. Liang
Gas Research Institute
8600 West Bryn Mawr Avenue
Chicago, IL 60631

No. of
Copies

W. G. Lindman
P.O. Box 567
Boyerstown, PA 19512

W. H. Link
Columbia Aluminum Corp.
85 John Day Dam Rd.
Goldendale, WA 98620

Steve Loftness
Washington State Energy Office
400 E. Union
Olympia, WA 98504

W. Long
Building B815
Dow Chemical
Freeport, TX 77541

R. A. Lowden
Metals and Ceramics Division
Oak Ridge National Laboratory
P.O. Box X, Bldg. 4515
Oak Ridge, TN 37831-6063

W. N. MacLay
Koppers Company, Inc.
440 College Park Drive
Monroeville, PA 15146

V. H. Markant
Du Pont
P.O. Box 787
Niagara Falls, NY 14302

C. J. McMinn
Extractive Metallurgical
Department
Reynolds Metals Company
P.O. Box 1200
Sheffield, AL 35660

C. H. McMurtry
Standard Oil Engineered
Materials Company
Niagara Falls R&D Center
P.O. Box 832
Niagara Falls, NY 14302

No. of
Copies

M. A. Mittnick
Avco Specialty Materials
Subsidiary of Textron Inc.
2 Industrial Avenue
Lowell, MA 01851

A. Moussa
A. D. Little, Inc.
20 Acorn Park
Cambridge, MA 02140

B. C. Mutsuddy
Battelle Columbus Division
505 King Avenue
Columbus, OH 43201-2693

A. N. Patel
Battelle Columbus Laboratories
505 King Avenue
Columbus, OH 43201-2693

J. R. Payne
Kaiser Aluminum and Chemical
Corp.
P.O. Box 877
Pleasanton, CA 94566

W. Pebley
Oregon Freeze Dry Corp.
525 25th Ave. S.W.
P.O. Box 1048
Albany, OR 97321

K. Peterson
Columbia Aluminum Corp.
85 John Day Dam Road
Goldendale, WA 98620

R. D. Peterson
Reynolds Metals Company
P.O. Box 1200
Sheffield, AL 35660

T. R. Prichett
Kaiser Aluminum and Chemical
Corp.
P.O. Box 877
Pleasanton, CA 94566

No. of
Copies

W. W. Pritsky
Aluminum Association
900 19th St. N.W.
Washington, DC 20006

S. P. Ray
Alcoa Technical Center
Alcoa Center, PA 15069

J. F. Rhodes
Advanced Composite Materials
Corp.
1525 S. Buncombe Rd.
Greer, SC 29651

N. E. Richards
Reduction Laboratory
Reynolds Aluminum Corporation
P.O. Box 1200
Sheffield, AL 35660

J. J. Ritter
Ceramics Division
National Bureau of Standards
Gaithersburg, MD 20899

R. C. Rohwedder
3028 Ohio Street
Longview, WA

J. Rosling
Myers Metals and Minerals
459 Colman Building
Seattle, WA 98104

D. R. Sadoway
MIT
Room 8-109
77 Massachusetts Avenue
Cambridge, MA 02139

W. Scott
Department of Materials
Science and Engineering
University of Washington
Wilcox Hall FB-10
Seattle, WA 98195

No. of
Copies

D. R. Secrist
Great Lakes Research Corp.
P.O. Box 1031
Elizabethton, TN 37643

A. B. Shah
Noranda Aluminum, Inc.
P.O. Box 70
New Madras, MO 63869

N. Shelton
Intalco
1300 S.W. 5th, Suite 3508
Portland, OR 97201

F. W. Spillers
Dow Chemical U.S.A.
B-1210 Building
Freeport, TX 77541

D. V. Stewart
Reynolds Metals Co.
P.O. Box 1200
Sheffield, AL 35660

D. Strahan
Reynolds Metals Company
P.O. Box 27003
Richmond, VA 23261

A. T. Tabereaux
Reynolds Metals Company
P. O. Box 1200
Sheffield, AL 35660

G. P. Tarcy
Aluminum Company of America
Alcoa Technical Center
Alcoa Center, PA 15069

P. Thaire
Primary Planning and Production
Alumax
400 S. El Camino Rd.
San Mateo, CA 94402

No. of
Copies

W. H. Thielbahr
Conservative Technology
Division
DOE-Idaho Operations Office
785 DOE Place
Idaho Falls, ID 83402

R. Unger
Merner Research
P.O. Box 248
Ridgewood, NJ 07451

A. Vinnard
Bonneville Power Administration
(KWI)
P.O. Box 3621
Portland, OR 97208

T. Von Müller-KWI
Bonneville Power Administration
P.O. Box 3621
Portland, OR 97208

D. H. Weinblatt
AIMCOR
One Parkway North
Deerfield, IL 60015

J. D. Weyand
Alcoa Technical Center
Alcoa Center, PA 15069

B. Wilcox
Northwest Aluminum Co.
3313 W. Second St.
The Dalles, OR 97058

C. B. Wilson
Dow Chemical U.S.A.
Texas Operations
B-101 Building
Freeport, TX 77541

W. Winnard
Battelle Washington Office
2030 "M" Street N.W.
Washington, DC 20036

No. of
Copies

J. C. Withers
Keramont Research Corporation
4233 S. Fremont Avenue
Tucson, AZ 85714

W. A. Zdaniewski
Engelhard Corporation
Menlo Park, CN28
Edison, NJ 08818

FOREIGN

D. Brodie
Comalco Ltd.
55 Collins St.
Melbourne, AUSTRALIA

T. Kjar
Comalco Ltd.
55 Collins St.
Melbourne, AUSTRALIA

E. W. Dewing
Alcan International
P.O. Box 8400
Kingston, Ontario
CANADA K7L 4Z4

T. J. Hudson
Alcan International
2001 rue University
C.P. 6090
Montreal, Quebec
CANADA H3C 3H2

D. N. MacMillan
Alcan International
C.P. 1250
Jonquiere, Quebec
CANADA G7S 4K8

T. Rawlings
Alcan International Limited
Engineering Division
C.P. 6090
Montreal, Quebec
CANADA, H3C 3H2

No. of
Copies

J. H. Reimers
Jan H. Reimers and Associates
Inc.
221 Lakeshore Road East
Oakville, Ontario
CANADA L6J 1H7

A. Oye
Institute of Inorganic
Chemistry
Norwegian Institute of
Technology
University of Trondheim
N-7034 Trondheim-NTH, NORWAY

J. Thonstad
Laboratories of Industrial
Electrochemistry
Norwegian Institute of
Technology
University of Trondheim
N-7034 Trondheim-NTH, NORWAY

K. O. Vee
ASV
Ardal Verk
N-5875 Ardalstargen, NORWAY

ONSITE

4 DOE Richland Operations Office

E. C. Norman

50 Pacific Northwest Laboratory

K. E. Bailey
M. Clement
M. Danielson
N. C. Davis
J. R. Divine
G. J. Exarhos
T. L. Gilbride
P. E. Hart

No. of
Copies

R. H. Jones
S. C. Marschman
G. L. McVay
N. L. Moore
C. H. Schilling (30)

No. of
Copies

D. M. Strachan
Publishing Coordination (2)
Technical Report Files (5)