Energy

**C
O
N
S
E
R
V
A
T
I
O
N**

DR # 0495-2
DOE/ID/12655-1
(DE88006572)

CERIUM OXIDE COATED ANODES FOR ALUMINUM ELECTROWINNING

Topical Report for the Period October 1, 1986—June 30, 1987

**By
J. K. Walker**

December 1987

Work Performed Under Contract No. AC07-86ID12655

**For
U. S. Department of Energy
Office of Industrial Programs
Washington, DC**

**By
ELTECH Research Corporation
Fairport Harbor, Ohio**

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 any of their employees, makes any warranty, express 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. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

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 any of their employees, makes any warranty, express 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. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Printed Copy A08
Microfiche A01

Codes are used for pricing all publications. The code is determined by the number of pages in the publication. Information pertaining to the pricing codes can be found in the current issues of the following publications, which are generally available in most libraries: *Energy Research Abstracts (ERA)*; *Government Reports Announcements and Index (GRA and I)*; *Scientific and Technical Abstract Reports (STAR)*; and publication NTIS-PR-360 available from NTIS at the above address.

CERIUM OXIDE COATED ANODES
FOR ALUMINUM ELECTROWINNING

Topical Report for Period
October 1, 1986 - June 30, 1987

by

J. K. Walker

December 1987

Work Performed Under Contract No. DE-AC07-86ID12655

Prepared for
U.S. Department of Energy
Idaho Operations Office, Idaho Falls, Idaho
Office of the Assistant Secretary for
Conservation and Renewable Energy
Office of Industrial Programs
Washington, DC

Prepared by
ELTECH Research Corporation
625 East Street
Fairport Harbor, Ohio 44077

TABLE OF CONTENTS

I. Summary	
A. Background	1
B. Objective	4
C. Scope	4
D. Technical Accomplishments	4
II. Background	5
III. In-Situ CEROX coatings	7
A. Introduction	7
1. Review of Previous Work	7
2. Review of ELTECH Technology	11
B. Materials and Methods	14
1. Materials	14
2. Laboratory Hall Cell	15
3. Coating Resistance Measurements	20
4. Analysis	21
5. Microscopy	22
6. Electrical Resistivity	23
7. Thermal Analysis	23
C. Thermodynamics of Ce in a Hall Cell Environment	25
1. Anodic Deposition of CEROX	25
a. Electrochemical Argument	25
b. Chemical Oxidation Argument	28
2. Cerium Partitioning	31
D. Testing of CEROX on SnO ₂	31
1. Coating Structure	32
2. Metal Analysis	43
3. Cerium Partitioning	48
4. CEROX Coating Resistance	50
E. Cermet Characterization	53
1. Chemical Analysis	55
2. X-ray Diffraction	55
3. Scanning Electron Microscopy	56
4. Thermal Properties	58
5. Electrical Resistivity	66

F.	Cermet Testing in Cerium-Free Bath	68
1.	Effect of Current Density	68
2.	Time Course Experiment	72
G.	Testing of Cermet in Cerium Containing Bath	78
1.	CEROX Coating	78
2.	Cerium Partitioning	82
3.	Coating Resistance	82
4.	Metal Purity	84
5.	Cermet Microscopy	89
H.	Time Course Tests of CEROX on Cermet	94
1.	Midpoint Conditions	94
2.	Preferred Conditions	104
I.	Bath Compositional Effects	113
1.	Alumina Concentration Effects	113
a.	Cerium Partitioning/Coating Development	113
b.	Coating Resistance	114
c.	Metal Purity	114
d.	Microscopic Examination	116
2.	Time Course Experiment in Low Alumina Bath	118
a.	CEROX Development	118
b.	Cermet Corrosion	121
3.	Effects of Bath Ratio	125
4.	Effect of LiF and MgF ₂ Additions	133
J.	Conclusions	136
K.	Recommendations	139
IV.	References	142

LIST OF FIGURES

1. SEM of Untested SnO ₂ Anode	16
2. Schematic of Bench-Scale Hall Cell	17
3. Diagram of Aluminum Reference Electrode	19
4. Predominance Diagram for Electrochemical Deposition of CEROX	27
5. Predominance Diagram for Oxidation of CeF ₃	29
6. Predominance Diagram for Oxidation of CeF ₃ AlF ₃ Activity = 5×10^{-4}	30
7. Scanning Electron Micrographs of CEROX Coatings on SnO ₂ at 0.8 A/cm ² . 0.5, 1.0 and 1.5% CeO ₂	33
8. Scanning Electron Micrographs of CEROX Coatings on SnO ₂ at 0.5% CeO ₂ . 0.8, 1.4 and 2.0 A/cm ²	34
9. Detailed Scanning Electron Micrograph of CEROX Coating on SnO ₂ (Area 1)	37
10. Detailed Scanning Electron Micrograph of CEROX Coating on SnO ₂ (Area 1)	38
11. Detailed Scanning Electron Micrograph of CEROX Coating on SnO ₂ (Area 2)	39
12. Detailed Scanning Electron Micrograph of CEROX Coating on SnO ₂ (Area 3)	40
13. Detailed Scanning Electron Micrograph of CEROX Coating on SnO ₂ (Area 4)	41
14. Percent Tin in Aluminum as a Function of CeO ₂ Concentration in Bath. 0.8 A/cm ²	45
15. Percent Tin in Aluminum as a Function of Current Density. 1.5% CeO ₂ Concentration	47
16. IR-free Anode Potential vs. log Current Density	51
17. Scanning Electron Micrograph of As-Received PNL 5324/ 17% Cu Cermet	57
18. Specific Heat of Cermet as a Function of Temperature	60

19.	Temperature Dependence of Cermet Thermal Diffusivity	61
20.	Temperature Dependence of Cermet Thermal Conductivity	62
21.	Thermal Expansion of PNL Cermet	64
22.	Temperature Dependence of the Mean Thermal Expansion Coefficient of the PNL Cermet	65
23.	Temperature Dependence of the Electrical Resistivity of the PNL Cermet	67
24.	Scanning Electron Micrograph of Cermet Tested in Cerium-Free Bath. 1.4 A/cm ²	70
25.	Percent Fe in Aluminum as a Function of Current Density. Cerium-Free Bath	71
26.	Percent Fe in Al as a Function of Time. Cerium-Free Time Course Experiment	73
27.	Total Fe in Al as a Function of Time. Cerium-Free Time Course Experiment	75
28.	Adjusted Weight Percent of Iron Deposited in Electrowon Aluminum. Cerium-Free Time Course Experiment	77
29.	Scanning Electron Micrographs of CEROX Coated Cermets as a Function of CeO ₂ Bath Concentration. 0.8 A/cm ²	79
30.	Scanning Electron Micrographs of CEROX Coated Cermets as a Function of CeO ₂ Bath Concentration. 1.4 A/cm ²	80
31.	Scanning Electron Micrographs of CEROX Coated Cermets as a Function of CeO ₂ Bath Concentration. 2.0 A/cm ²	81
32.	Effect of Nominal CeO ₂ Bath Concentration on Fe and Cu Levels in Aluminum. 0.8 A/cm ²	86
33.	Effect of Nominal CeO ₂ Bath Concentration on Fe and Cu Levels in Aluminum. 1.4 A/cm ²	87
34.	Effect of Nominal CeO ₂ Bath Concentration on Fe and Cu Levels in Aluminum. 2.0 A/cm ²	88
35.	Total Fe in Recovered Al as a Function of Current Density.	90
36.	Backscattered SEM of CEROX Coated Cermet with Reaction Layer. 1.4 A/cm ² ; 1.0% CeO ₂ in Bath.	92
37.	X-Ray Maps of Reaction Layer in CEROX Coated Cermet	93
38.	Percent Cerium in Bath and Aluminum as a Function of Time. 1.4 A/cm ² ; 1.0% CeO ₂ Bath Concentration.	95

39.	Total Weight of Cerium in Bath and Aluminum as a Function of Time. 1.4 A/cm ² ; 1.0% CeO ₂ Bath Concentration.	96
40.	Weight Percent Fe in Aluminum pool as a Function of Time. 1.4 A/cm ² ; 1.0% CeO ₂ Bath Concentration.	98
41.	Total Weight of Fe in Aluminum as a Function of Time. 1.4 A/cm ² ; 1.0% CeO ₂ Bath Concentration.	99
42.	Comparison of Time Course Experiments Performed at 1.4 A/cm ² . No Cerium and 1.0% CeO ₂	101
43.	Adjusted Weight Percent of Iron Deposited in Electrowon Aluminum. 1.4 A/cm ² ; 1.0% CeO ₂ Bath Concentration.	102
44.	Scanning Electron Micrographs of CEROX Coated Cermets as a Function of Time with Reaction Layer. 1.4 A/cm ² 1.0% CeO ₂	103
45.	Percent Cerium in Bath and Aluminum as a Function of Time. 0.8 A/cm ² ; 1.5% CeO ₂ Bath Concentration.	105
46.	Total Weight of Cerium in Bath and Aluminum as a Function of Time. 0.8 A/cm ² ; 1.5% CeO ₂ Bath Concentration.	106
47.	Weight Percent Fe and Cu in Aluminum pool as a Function of Time. 0.8 A/cm ² ; 1.5% CeO ₂ Bath Concentration.	108
48.	Total Weight of Fe and Cu in Aluminum as a Function of Time. 0.8 A/cm ² ; 1.5% CeO ₂ Bath Concentration.	109
49.	Adjusted Weight Percent of Iron Deposited in Electrowon Aluminum. 0.8 A/cm ² ; 1.5% CeO ₂ Bath Concentration.	110
50.	Scanning Electron Micrographs of CEROX Coated Cermets as a Function of Time. 0.8 A/cm ² ; 1.5% CeO ₂	112
51.	Percent Fe and Cu Levels in Aluminum as a Function of Bath Alumina Concentration. 0.8 A/cm ² 1.5% CeO ₂	115
52.	Optical Micrographs of CEROX Coated Cermets at Varying Bath Alumina Concentration. 0.8 A/cm ² 1.5% CeO ₂	117

53.	Percent Cerium in Bath and Aluminum as a Function of Time. 0.8 A/cm ² ; 1.5% CeO ₂ 4.0% Alumina Bath Concentration.	119
54.	Total Weight of Cerium in Bath and Aluminum as a Function of Time. 0.8 A/cm ² ; 1.5% CeO ₂ , 4.0% Alumina Bath Concentration.	120
55.	Scanning Electron Micrographs of CEROX Coated Cermets as a Function of Time. 0.8 A/cm ² ; 1.5% CeO ₂ ; 4.0% Alumina Bath Concentration.	122
56.	Weight Percent Fe and Cu in Aluminum as a Function of Time. 0.8 A/cm ² ; 1.5%, CeO ₂ , 4.0% Alumina Bath Concentration.	124
57.	Total Weight of Fe and Cu in Aluminum as a Function of Time. 0.8 A/cm ² ; 1.5% CeO ₂ , 4.0% Alumina Bath Concentration.	126
58.	Comparison of Time Course Experiments Performed at 0.8 A/cm ² and 1.5% CeO ₂ Concentration. 8.0% and 4.0% Alumina in Bath.	127
59.	Adjusted Weight Percent of Iron Deposited in Electrowon Aluminum. 0.8 A/cm ² ; 1.5% CeO ₂ ; 4% Alumina Bath Concentration.	128
60.	Scanning Electron Micrographs of CEROX Coated Cermets Produced with Baths of Differing Ratio. 0.8 A/cm ² 1.5% CeO ₂	130
61.	Scanning Electron Micrographs of CEROX Coated Cermets Produced with Bath Containing LiF and Both LiF and MgF ₂ . 0.8 A/cm ² ; 1.5% CeO ₂	135

LIST OF TABLES

1. Effect of Current Density and CeO_2 Concentration on CEROX Coating Thickness	36
2. Microprobe Analysis of CEROX on SnO_2 Figures 9-13	42
3. Tin and Copper Levels in Aluminum pool as a Function of Current Density and CeO_2 Bath Levels	44
4. Partition Coefficient for Cerium in SnO_2 Trials	49
5. CEROX Coating Resistance as a Function of Current Density and CeO_2 Bath Concentration	54
6. Thermal Conductivity of PNL Cermet as a Function of Temperature	59
7. Thermal Expansion of PNL Cermet	63
8. Metal Analysis from Cermet Runs in Cerium-Free Bath	68
9. Cerium Partition Coefficients for Cermet Trials	83
10. CEROX Coating Resistances Determined in Cermet Trials	85
11. Cerium Partition Coefficients as a Function of Alumina Concentration in the Bath	114
12. Effect of Bath Ratio and LiF and MgF_2 Bath Additions of Purity of Aluminum.	129
13. Effect of Bath Ratio on Cerium Partition Coefficients	132

CEROX COATED ANODES FOR ALUMINUM PRODUCTION

I. SUMMARY

A. Background

In the conventional Hall-Heroult process, anode carbon is consumed according to the reaction

with the side reaction

Although, according to reaction (1), 0.33 kilogram of carbon is theoretically required for each kilogram of aluminum, the actual consumption is nearly 0.5 kilogram. The exit gas from a Hall-Heroult cell may contain 10 to 50% CO (1). Loss of carbon may also be caused by selective oxidation, cracking and arcing. Because of metal purity considerations, a relatively pure coke with low ash content must be used as anode carbon. Additionally, non-uniform wear of the carbon anode imposes an energy penalty because an even interelectrode gap cannot be maintained.

Because of the cost of building and maintaining a carbon anode plant and the energy penalties associated with the use of carbon anodes, the use of inert anodes has long been proposed (2,3). With an inert anode, the net cell reaction is

The reversible potential for this reaction at 1000°C is 2.2 V compared to 1.15 V for the conventional process. Despite this, a net energy savings is anticipated with the use of inert anodes (4). The major savings would be in petroleum coke and its energy

content. It has been estimated that U.S. consumption of petroleum coke for anode carbon is at 2.27 million metric tons per year (5). A lower anode overpotential with an inert anode may also produce an energy savings.

A major savings associated with the use of an inert anode is anticipated from improvements in cell design and operation. Alcoa has estimated that if the anode-cathode gap could be lowered from the present 4.4 cm to 1.9 cm, a 23% decrease in the energy requirement would be achieved (5). Additional energy savings may also result from reduced pollution control costs and improved structural drops.

The material requirements of an inert anode in an aluminum reduction cell include: a) low solubility in the molten cryolite bath, b) oxidation resistance, c) thermal shock resistance, d) high electrical conductance compared to carbon, e) low oxygen overpotential, and f) adequate mechanical strength (2,3). In addition to these requirements, the material must be low cost and easily fabricated into large shapes.

Early work on inert anodes has concentrated on metals and ceramic oxides. Metals generally have high electrical conductivity, but with the exception of some of the precious metals, were subject to massive oxidation. Some of the oxide ceramics have been found to have very low solubility in cryolite melts, but generally possess low conductivities. It is generally acknowledged that no metal oxide has been found to meet the requirements of an inert anode.

In recent years, various cermet anodes, developed by Alcoa (5), have received considerable attention. By including a metallic phase in the ceramic matrix, high electrical conductivity cermets have been obtained while maintaining the corrosion-resistant properties of the ceramic. The most promising results were obtained with a material containing a nickel ferrite matrix and 17% Cu metal. With this cermet, targeted dissolution rates were obtained in laboratory tests. However, these have not been demonstrated in pilot scale tests.

In the past several years, ELTECH Systems Corp. has demonstrated the anodic deposition of a cerium oxyfluoride (CEROX) from conventional Hall-Heroult cryolite melts (6). This led to the proposed use of CEROX as a self-forming anode, deposited in-situ. The significance of this concept is that it provides a mechanism for protection of an anode substrate against corrosive attack.

During the course of the present program, the anodic deposition of CEROX coatings on both tin oxide and on the copper containing nickel ferrite was studied. Tin oxide substrates were employed because of ELTECH's extensive laboratory experience with this material, whereas the copper containing nickel ferrite was employed because it is, at present, the leading inert anode candidate. The results of our study have demonstrated the CEROX coatings produced in-situ decrease the attack on both tin oxide and the copper-containing nickel ferrites. It is anticipated that the decreased attack would result in an increased life of the anode substrate. This could make possible the successful

implementation of an inert anode technology for aluminum production. The experimental results will be represented in the following sections of the report.

B. Objective

The overall objective of this research was to establish a technical data base on the chemical and physical properties of substrates and anodically deposited coatings for use as electrodes in Hall-Heroult cells. The successful development of a coated anode will produce aluminum of acceptable purity and should result in an energy savings over the present Hall cell operation.

C. Scope

The primary scope of this program was directed toward in-situ deposition of cerium oxyfluoride (CEROX) on antimony doped tin oxide and nickel ferrite/copper cermet anode substrates. Corrosion resistance of the coated structures was evaluated by microstructural analysis and by chemical analysis of the aluminum metal. Cerium mass balances were also performed to determine the effect of experimental variables on the cerium concentration in the aluminum. The electrical resistance of the coatings was also assessed by monitoring the change in the iR component of the anode potential.

D. Technical Accomplishments

In the present study, it has been demonstrated that cerium oxide coatings (CEROX) can readily be deposited on both SnO_2 and copper containing nickel ferrite cermets from conventional Hall-Heroult electrolytes. The deposition of the coating is controlled by the equilibrium between CeO_2 and the bath components

AlF_3 , Al_2O_3 and CeF_3 . The coating thickness was found to be primarily dependent on the amount of cerium added to the bath. However, other factors such as current density and bath ratio affect both the coating thickness and coating morphology.

With both tin oxide and the copper/ferrite cermet, the presence of a cerium oxide coating was shown to decrease attack on the substrate. The thickest coatings, produced at low current density and high initial cerium bath concentration were the most protective. However, under all conditions, the CEROX coating diminished attack on the anode substrate. With a CEROX coating deposited under optimum conditions, the cermet corrosion could not be detected in our ten hour tests. In contrast, corrosion of the uncoated cermet in cerium-free bath was readily apparent.

A voltage increase could be attributed to the presence of the CEROX coating. The most protective coatings were found to be the most resistive. Therefore, it is likely that in commercial practice, a trade-off between substrate wear and voltage will be possible. Because the CEROX coating reduces anode wear at high current densities, it may be possible to achieve an acceptable anode life while operating at higher current density. Therefore, another trade-off may also exist between higher production rates and voltage.

II. BACKGROUND

The use of dimensionally stable anodes for aluminum electrowinning has been considered since the time of Hall's original work and has been the subject of considerable research (2,3). Inert anodes offer the promise of operating cost savings by elimination of the consumable

carbon anode and by a lower cell voltage, achieved by reduction of the anode-cathode distance and reduction of the anode polarization. The energy requirement for the conventional Hall-Heroult cell is summarized below (7).

Energy Requirement for Hall-Heroult Process

1. Thermodynamic Potential	1.2 V
2. iR Loss in Bath	1.9 V
3. Anode Polarization	.5 V
4. iR Loss in Electrodes and Current Collections	<u>.9</u>
Total Cell Voltage	4.5

Although the reversible potential for a dimensionally stable oxygen anode is approximately one volt greater than that of a carbon anode, this can be more than offset by a lower overvoltage and lower ohmic losses. The polarization requirement for an inert anode has been reported to be .2 V less than that of a carbon electrode (2). In addition, the conductivity of cermet anodes may reach three times that of carbon (8) and would greatly reduce ohmic losses in the anode. The use of an inert anode, in combination with a wettable cathode, also offers the potential of reducing the interelectrode distance, greatly lowering the ohmic drop in the electrolyte. The development of a more compact cell design may also result from this technology. The energy requirement for a Hall-Heroult cell using inert anodes is summarized below. It is assumed that the anode-cathode gap is half that used in the conventional process.

Energy Requirement for Hall-Heroult Cell with Inert Anode

1. Thermodynamic Potential	2.20 V
2. iR Loss in Bath	1.00 V
3. Anode Polarization	0.30 V
4. iR Loss in Electrodes and Current Collectors	<u>0.90 V</u>
Total Cell Voltage	4.40 V

The material properties required of an inert anode in an aluminum reduction cell include (2):

1. Insolubility in the molten fluoride melt.
2. Oxidation resistance.
3. Thermal shock resistance.
4. Electrical resistivity less than or comparable to carbon.
5. Low oxygen overpotential.

III. IN-SITU CEROX COATINGS

A. Introduction

1. Review of Previous Work

The use of inert anodes in aluminum reduction cells has been proposed since the time of Hall's initial invention. Indeed, Hall himself devoted a great deal of effort in the pursuit of an oxygen anode. Unfortunately, the problems initially encountered, i.e., metal contamination, anode life, conductivity and cost, persist to this day. Past efforts to develop an inert anode have been reviewed by Billehaug and Oye (2). More recent efforts have largely concentrated on cermet materials in work carried out at Alcoa. A summary of previous work is presented below.

Metal Anodes

Although platinum group metals may meet these criteria (2), the prohibitive cost would preclude their use. Less noble metals are generally not suitable as inert anodes. Belyaev and Studentsov (9,10) found that copper, nickel, chromium, and silver were not resistant to oxygen. The oxide layers which formed spalled off, exposing fresh metal surfaces to be attacked. Kronenberg (11) also found copper and nickel to be severely attacked under anodic polarization. Copper anodes, which were originally suggested by Hall, have been tested on an industrial scale with no success (12).

Boride, Carbide, and Nitride Anodes

Refractory metal borides, carbides and nitrides have been proposed as anodes. However, studies with these materials have shown that in all cases, these have corroded badly during electrolysis (13).

Metal Oxide Anodes

Because of their stability in the presence of oxygen, oxide ceramics have also been studied as inert anodes for aluminum electrowinning by the Hall-Heroult process. However, all candidate materials examined to date have exhibited a finite solubility in the cryolite melt which leads to unacceptably high contamination levels of the electrowon aluminum. Moreover, the least soluble oxides are thermodynamically unstable with respect to aluminum which is found dissolved in the electrolyte. These problems have presented the major obstacle in the development of the

dimensionally stable anode technology.

Early investigations by Belyaev and Studentsov (9) identified Fe_3O_4 , SnO_2 , NiO and ZnO as the oxides having the lowest solubility in molten cryolite and the highest stability in laboratory polarization tests. The rate of corrosion of a Fe_3O_4 anode was found to be independent of current density. The electrowon aluminum was also found to contain up to 1.5% iron.

In a subsequent study, Belyaev (14) found that ferrites such as NiOFe_2O_3 and ZnFe_2O_4 had higher electrical conductivity and better corrosion resistance than the pure oxides. Since then, a large number of patents have issued describing the use of metal oxide and mixed metal oxides as inert anodes. However, in nearly all cases, the most serious problem continues to be the dissolution of the oxide into the cryolite (3), and in turn, the contamination of the electrowon aluminum.

Of the oxides considered, SnO_2 has received the most attention because of low solubility (2) and high electrical conductivity, achieved by doping. Unfortunately, unacceptably high levels of tin in the aluminum product have been observed repeatedly (15). It has been proposed that the corrosion of the SnO_2 is through chemical attack by dissolved aluminum, which may be present at a level of several tenths of a percent (16,17). Various engineering approaches have been attempted to reduce SnO_2 corrosion (15,18,19), including oxygen protection. However, none of these approaches have been

adopted commercially. It is generally acknowledged that a more rugged anode needs to be developed. SnO_2 does have a large data base on its performance and does provide a valuable control substrate that is readily available.

Cermet Anodes

In 1982, Alcoa (20) disclosed the development of a cermet anode composed of 70% $\text{NiFe}_2\text{O}_4/\text{NiO}$ and 30% Ni metal. Both the ceramic phase and metal phase were continuous in this material. The $\text{NiFe}_2\text{O}_4/\text{NiO}$ had low chemical solubility in cryolite. The Ni metal phase improved both the electrical conductivity of the material and improved its mechanical properties, such as thermal shock resistance.

Rapid development of this material led to the eventual testing in a 2500 amp pilot cell (8). Although failure of the test after 21 days of operation was attributed to degradation of the cermet/steel conductor connection, an autopsy of the tested anode revealed that microstructural changes in the cermet precluded extended operation of the cell. Later studies indicated that corrosion of the Ni phase by oxidation or electrolysis occurs during operation, causing cracking and bath penetration.

The leaching of the metal phase from the cermet led Tarcy (21) to screen various pure metals and commercially available alloys to find a material with a higher polarization requirement for anodic dissolution than nickel. Although none of the metals or alloys tested, other than platinum, were sufficiently resistant to serve as an inert anode alone,

copper and copper/nickel alloys were proposed to be promising candidates for a metal phase in the cermet. It was found that the passivating layer on Cu and Cu/Ni alloys tends to spall off the surface of a metal surface, but not when incorporated into the ceramic matrix.

Subsequently, Ray (22) developed a new cermet material in which the Ni-Fe alloy is replaced by Cu-Ni-Fe. It was reported that this material does not degrade with time and forms a passive layer which prevents loss of the metallic phase.

A series of cermet materials containing 83 - 95% metal oxide and 5 - 17% Cu metal was examined in 30 hour laboratory bench tests (23). The aluminum produced contained impurities of 0.03 - 0.07% Ni, .26 - .34% Fe and 0.05 - 0.12% Cu. These levels fall within the Alcoa target of total impurities less than 0.5%.

Recently, the development of the copper containing nickel ferrite has continued at Battelle's Pacific Northwest Laboratories. Processing of the cermet has been refined to minimize anode wear. In addition, the effect of various bath chemistries has been examined. Long-term testing of the improved cermet material is planned to establish wear rates and projected lifetimes.

2. Review of ELTECH Technology

ELTECH Systems Corporation has been actively involved in research for inert anodes for aluminum electrowinning since the mid-1970's. The program initially involved the screening of

various oxide ceramics (including SnO_2) and cermets. Several promising candidates were identified (24,25), although unacceptable high corrosion rates would prevent their use commercially.

The recent development of the CEROX coating technology can be traced back to late 1982, when it was accidentally discovered that cerium dioxide could be anodically deposited from a molten cryolite electrolyte. When one weight percent cerium oxide was added to a conventional Hall cell bath, it was noted that a 1 mm thick gray-blue layer was formed on the surface of a palladium anode. Subsequent x-ray diffraction of the coating confirmed the major phase to be cerium dioxide (CEROX), with cryolite detected as a minor phase. Mass balance calculations also demonstrated that most of the cerium added to the system was deposited at the anode as cerium oxide. The deposition of the CEROX coating was later found to be quite reproducible and applicable to both metallic and ceramic substrates. The first patent describing the CEROX coating technology was recently issued (26).

Thermodynamic studies predict that the anodic formation of cerium dioxide is attributed to the oxidation of a cryolite soluble cerrous oxyfluoride coupled with the precipitation of ceric oxide at the anode surface.

This is analogous to the mechanism of anodic deposition of manganese dioxide in aqueous systems. Electrochemical studies have indicated that the oxidation of cerium (III) to cerium (IV)

occurs at a potential which is slightly anodic relative to oxygen evolution. Therefore, these reactions should occur simultaneously under aluminum electrowinning conditions.

In our preliminary studies, various materials, both metallic and ceramic, have been evaluated as substrates. Because of the anodic potential at which CEROX deposition occurs, only metallic or ceramic substrates electrochemically stable at oxygen evolving potentials (e.g., Pd, Pt) were found to be suitable substrates. CEROX deposition was observed on the metal oxide ceramic substrates studied (doped tin oxide, nickel ferrite), although the poor conductivity of the pure ferrite sample generally resulted in a non-uniform coating. Substrates with high porosity also produced less uniform coatings. It is anticipated that, because of the physical properties of the copper containing nickel ferrite, more uniform coatings should be produced on this substrate.

Preliminary results indicate that two primary factors influence the thickness of the CEROX coating: current density and cerium concentration in the cryolite melt. The CEROX coating thickness appears to increase with current density up to 1.2 A/cm², the upper limit of current density examined to date. The most dense coating appears to occur at a somewhat lower current density, although this varies with the porosity of the substrate. The coating thickness is also affected by the cerium content in the melt. The coating thickness increases nearly linearly with the nominal cerium concentration in the melt.

Significantly, it has been observed that the cerium oxide coating affords protection to the substrate against corrosive attack. An indirect measure of dissolution of tin oxide can be obtained by determining the Sn concentration in the electrowon aluminum. Using a cerium oxide coating, the Sn contamination resulting from dissolution of SnO_2 has been reduced by up to three orders of magnitude in laboratory tests. Although this effect was previously demonstrated only with SnO_2 anodes, it was expected that the cerium oxide coating would afford protection independent of the substrate material.

Although cerium oxide coatings do reduce the rate of corrosion of the anode substrate, the coating is not impervious. Therefore, a key to attaining long life and stable performance is the identification of a stable substrate. Because of its low corrosion rate, the copper-containing nickel ferrite cermet was selected for further study. The evaluation of CEROX coated cermet anodes was therefore the major objective of this program.

B. Materials and Methods

1. Materials

Synthetic cryolite from American Fluoride Co. (Lot 1178 Fine Powder No. 1-680) was used as received in all experiments. Anhydrous aluminum oxide, 99% purity, (Certified Lot A-591) and calcium fluoride, 99.9% purity (Lot C-89) were obtained from Fisher Scientific Co. Prior to use, these were dried at 700°C under vacuum (100 mtorr) for 24 hours. Cerium oxide (Lot C-578), 99.5% purity, was also obtained from Fisher Scientific. Anhydrous aluminum fluoride (Lot A-1115) was

purchased from Cerac Inc. and was greater than 99.9% purity.

The tin oxide anode material was provided by Corning Glass (T-1185 SnO₂; Lot J8-3 14-4). This material was developed for use as electrodes in glass melting furnaces. The batch used had the following composition:

Sb ₂ O ₅	0.96%
CuO	0.53%
SnO ₂	Approximately 98.5%

As shown in Figure 1, the copper oxide is found primarily as discreet phases in pores and between SnO₂ grains (see spots A, B, and C). Spot D in the micrograph corresponds to SnO₂.

The copper-containing nickel ferrite was prepared and supplied by Pacific Northwest Laboratories. Characterization of this material is described in a later section.

2. Laboratory Hall Cell

All anode tests were performed in a bench-scale Hall cell, shown in Figure 2. Alumina crucibles (McDanel Alumina grade 998, 99.8% purity) were used to contain the electrolyte. Alumina was fed to the cell from a hopper at the top of the cell. Molten aluminum in an alumina cup served as the cathode in all experiments. An alumina sheathed, graphite rod was used to make the connection. In experiments in which the alumina concentration was varied, all alumina cell components were replaced with aluminum nitride (Cerac Inc.).

SEM of untested SnO₂ anode

SEM/EDX microprobe semi-quantitative results

SnO₂ T-1185

Spot Position	Approx. Met. Comp. as Wt. Percent		
	Cu	Sn	Sb
A	98	2	0
B	99	2	0
C	92	8	0
D	0	100	0

Figure 1. SEM of Untested SnO₂

Figure 2. Schematic of Bench-Scale Hall Cell

Alumina additions were made during the test at 2 hour intervals. The nominal cerium oxide additions were adjusted to take into account the cerium concentration in the aluminum which was predetermined from partition coefficients.

Except as otherwise stated, the test electrolyte consisted of cryolite, adjusted with aluminum fluoride to a ratio of 1.35, with nominal additions of 8% alumina and 5% calcium fluoride.

The aluminum reference electrode was basically that recommended by Piontelli (27) and recently discussed by Burgman, Leistra and Sides (28). An aluminum pool was contained in a sintered alumina tube, with an alumina sheathed Mo rod used to make the electrical connection. A small hole was drilled in the alumina tube to provide for a liquid junction, although it has been reported that this is unnecessary (28). The stability of this type of reference electrode has been reported to be 3 - 5 mV (28).

All anode substrates used in this work were 1.9 cm in diameter. The anodes were sheathed in an alumina tube (McDanel Alumina grade 998, 99.8% purity), which was secured with an alumina pin. The sheathing of the anodes was to mask off the anode sides, thereby limiting the active surface area to the bottom face. In experiments in which the alumina concentration was varied, aluminum nitride sheaths were substituted. Connections to the anodes were made mechanically by threading a 1/8" inconel rod into a graphite rod insert at the top of the anode (see Figure 3).

Figure 3. Diagram of Alumina Reference Electrode

The entire bench-scale Hall cell was operated in an inconel retort. A graphite protection crucible was used to protect the retort from spilled bath. The retort walls were lined with refractory rings (North American Refractories) to prevent the contamination of the bath by scaling of the retort material. Similarly, a graphite plate insert was used beneath the retort lid to prevent contamination of the bath by scaling of the inconel. The retort was heated in a crucible furnace (Lindberg Model 56000 with a type 1000 controller), which can be controlled to within 1°C. The temperatures were measured with an alumina sheathed chromel-aluminel thermocouple. The furnace was brought up to temperature in 4 hours and the system allowed to equilibrate for 2 hours before start of the experiment.

Sorenson DCR 40-25B power supplies were used as the constant current source. The currents were measured by the voltage drop across a standard 1 ohm resistor (Dale Electric, accurate to within 1%). Voltage measurements were made with a Keithley 179A multimeter and monitored throughout the run with a YEW Model 3061 Multipen recorder.

3. Coating Resistance Measurements

The measured potential difference between the anode and reference electrode always contains an iR component with contributions from the electrolyte, oxide coating, anode substrate, etc. This total iR component was measured using a current interrupt technique, as described by Mcleod, Haggerty and Sadoway (29). The current interrupter was manufactured by

MS Industries. The potential decay transients following current interruption were measured with a Nicolet Model 3091 digital oscilloscope. The iR-free anode potentials were obtained by subtracting the measured iR component from the measured anode potentials.

Polarization curves were performed in two hour intervals throughout the experiments. The resistivity of the cerium oxide coating was determined from the increase in the iR component of the anode potential from zero time.

The iR component of the anode potential was also determined by means of a differential Tafel plot of measured potentials. This method is based on the fact that the measured anode potential is the sum of the anode potential and the resistance terms.

$$V = E_d + E_a + iR$$

where: V = measured anode potential

E_d = decomposition potential

E_a = anodic overpotential = $A \ln i + B$ (Tafel eq.)

i = current

Differentiating the equation with respect to i yields:

$$dV/di = A/i + R$$

Therefore, the intercept of the plot of $\Delta V / \Delta i$ vs. A/i is equal to the resistance in the measurement.

4. Analysis

Upon completion of the test, the anode was withdrawn from the bath and the cell allowed to cool. Cryolite and aluminum

samples were obtained, and elemental analysis was performed by Ricerca Inc., Concord, Ohio.

Cryolite samples were first crushed with a mortar and pestle and weighed in a platinum crucible. The specimens were then dissolved into a molten mixture of $\text{Na}_2\text{CO}_3/\text{H}_3\text{BO}_3/\text{K}_2\text{CO}_3$. The fused salt was then dissolved in HCl in a Teflon beaker and diluted in a volumetric flask. Analysis was performed by ICP using a standard addition method.

Analysis of the aluminum was performed in a similar manner. The aluminum was first dissolved in HCl and H_2SO_4 . Insoluble material was collected and treated with a molten $\text{Na}_2\text{CO}_3/\text{H}_3\text{BO}_3$ bath. The solutions were combined, diluted, and also analyzed by ICP.

5. Microscopy

Cerium oxide coated anode specimens were sectioned with a Beuhler diamond cut-off saw. The specimens were sectioned perpendicular to the deposition plane and then mounted in epoxy in prenumbered phenolic ring forms. These were subsequently ground and polished with diamond paste starting from 15 μ down to 0.1 μ .

Optical microscopy was performed with a Nikon Optiphot microscope. Both polarized and unpolarized optical microscopy were carried out in order to identify the various phases and determine their distribution.

Scanning electron microscopy was performed using a JEOL 35 CX. Back scatter electron imaging (BSEI) was used to identify the topology of phase distribution on the substrate/coating

interface based on the compositional variation.

Semiquantitative and quantitative information concerning the composition of phases was gathered by use of both energy dispersive spectroscopy (EDS) and wavelength dispersive spectroscopy (WDS). X-ray mapping was carried out to qualitatively provide elemental distribution in different phases.

6. Electrical Resistivity

The electrical resistivity of the copper-containing nickel ferrite was determined in the temperature range of 25°C to 1000°C. Measurements were made using a flowing Ar atmosphere. A four-point test apparatus was used in which contact pressure was achieved by compression springs which are screw adjusted. Temperature control, current pulse, and voltage frequency were computer controlled.

7. Thermal Analysis

All thermal characterization of the copper-containing nickel ferrite was performed at the Thermal-Physical Research Laboratory of Purdue University. The properties determined were specific heat, thermal diffusivity, thermal conductivity and thermal expansion.

Specific heat, C_p , was measured using a standard Perkin-Elmer Model DSC-2 Differential Scanning Calorimeter using sapphire as a reference material. The standard and sample were subjected to the same heat flux, and the differential power required to heat the sample at the same rate was recorded using the digital data acquisition system.

From the mass of the sapphire standard and the mass of the pans, the differential power, and the known specific heat of sapphire, the specific heat of the sample was computed.

Thermal diffusivity was determined using the laser flash diffusivity method. According to this method, the front face of a small disc-shaped sample is subjected to a short laser burst and the resulting rear face temperature rise is recorded. The apparatus consists of a Korad K2 laser, a high vacuum system including a bell jar with windows for viewing the sample, a tantalum tube heater surrounding a sample holding assembly, a spring-loaded thermocouple or an iR detector, appropriate biasing circuits, amplifiers, A-D converters, crystal clocks and a minicomputer-based digital data acquisition system capable of accurately taking data in the 40 microsecond and longer time domain. Thermal conductivity was calculated as the product of diffusivity, specific heat and density.

A dual Push-Rod Dilatometer (Theta Dilatronics II) was used to measure linear thermal expansion. The differential expansion between the sample and a known standard reference material was measured as a function of temperature. The expansion of the sample is computed from this differential expansion and the expansion of the standard. The measurements were made under computer control, and the linear expansion was calculated at preselected temperature intervals.

C. Thermodynamics of Ce in a Hall Cell Environment

1. Anodic Deposition of CEROX

In order to define the equilibria involved in the deposition of CEROX, the thermodynamics of the Ce, Al, Na, O, F system has been examined. The anodic deposition of CEROX can be effectively described as either an electrochemical or chemical process. Therefore, both cases are presented here.

a. Electrochemical Argument

The electrochemical deposition of CeO_2 can be expressed as the following two half reactions:

The net reaction would be:

The ΔG° for this reaction at 1300°K is 141390 cal., which corresponds to an applied EMF of 3.06 V.

The anodic deposition of CeO_2 is, of course, in competition with the oxygen evolution reaction.

Equation (5) has a free energy change of 301680 cal., corresponding to an applied EMF of 2.18 V.

Based only on standard free energy change, it would appear that CeO_2 deposition would never occur. However, it must be noted that ΔG for equation (4) is influenced by the AlF_3 activity, which in pure cryolite

has been estimated to be between 10^{-5} and 10^{-3} (1). In a cryolite bath with ratio 1.35, Dewing and Yoshida estimated the AlF_3 activity to be 5×10^{-3} (17).

In order to visualize the dependence of CeO_2 deposition on AlF_3 activity and applied potential, a predominance diagram (Figure 4) was constructed. All species other than AlF_3 were assumed to be in their standard state. In addition to equation (4), the following equilibria were considered:

$$1300^\circ\text{K} \text{ } \Delta G^\circ = 86559 \text{ cal}$$

$$1300^\circ\text{K} \text{ } \Delta G^\circ = 54830 \text{ cal}$$

$$1300^\circ\text{K} \text{ } \Delta G^\circ = -65734 \text{ cal}$$

$$1300^\circ\text{K} \text{ } \Delta G^\circ = -44910 \text{ cal}$$

As can be seen in the figure, at AlF_3 activities less than 10^{-3} , the deposition of CeO_2 becomes thermodynamically possible at normal O_2 evolving potentials in pure cryolite. CeO_2 deposition is not possible at CO_2 evolving potentials at practical AlF_3 activities. It is also predicted that at very acidic conditions (high AlF_3 activity), CeO_2 deposition is not favored at O_2 evolving potentials.

In summary, CeO_2 deposition is possible largely because of the low AlF_3 activity in cryolite melts. In normal acidic melts, deposition can occur at high O_2

Figure 4. Predominance Diagram for Oxidation of CeF₃

overpotentials.

b. Chemical Oxidation Argument

Cerium oxide deposition could possibly occur by chemical oxidation of CeF_3 .

$$1300^\circ\text{K} \text{ } \Delta G^\circ = 40892 \text{ cal}$$

From the large, positive value of ΔG° , it is clear that with all species in the standard state, the reaction is not spontaneous. However, in a cryolite melt, the activity of AlF_3 can be quite low, shifting the equilibrium to the right.

Figure 5 shows a predominance diagram for the Ce, Al, Na, O, F system at 1300°K , plotting the $\log \text{Al}_2\text{O}_3$ activity vs. the $\log \text{O}_2$ pressure. An activity of 10^{-5} was assumed for AlF_3 . The activity of $\text{Na}_3 \text{AlF}_6$ was set at 0.3. As would be expected, CeO_2 formation is favored at high Al_2O_3 activity and O_2 pressure. At 1 atmosphere O_2 , the critical Al_2O_3 activity is 3×10^{-4} .

For comparison, an identical diagram was constructed assuming an AlF_3 activity of 5×10^{-4} (Figure 6). In this case, more oxidizing conditions are required to form CeO_2 . At 1 atm. O_2 , the critical Al_2O_3 activity is approximately 0.3.

Just as with the electrochemical oxidation, the chemical oxidation of CeF_3 to CeO_2 is possible only because of the low activity of AlF_3 in cryolite. In acidic melts, CeO_2 deposition is less likely. High Al_2O_3

$$a(\text{AlF}_3) = 10^{-5}$$

$$a(\text{Na}_3 \text{AlF}_6) = .3$$

Figure 5. Predominance Diagram for Oxidation of CeF_3 , AlF_3
Activity = 10^{-5}

Figure 6. Predominance Diagram for Oxidation of CeF_3 , AlF_3
 Activity = 5×10^{-4}

activity and O₂ pressure promote oxidation.

2. Cerium Partitioning

In a Hall-Heroult cell using CEROX coated anodes, an equilibrium is expected to be established between the Ce in the aluminum and CeF₃ in the melt.

$$1300^\circ\text{K} \quad \Delta G^\circ = 66047 \text{ cal}$$

According to this equation, with the reactants and products in their standard state, Al will not reduce CeF₃. However, the formation of intermetallics, e.g., CeAl₄ and CeAl₂ would lower the Ce activity in Al and promote reduction of CeF₃.

The distribution of Ce in the Al and the melt should be determined by the equilibrium established by the above reaction.

$$K_{\text{eq}} = a_{\text{Ce}} \times a_{\text{AlF}_3} / a_{\text{CeF}_3} \times a_{\text{Al}} \quad (12)$$

assuming the activity of AlF₃ and Al should be constant. Therefore, we can define a partition coefficient as the ratio of Ce in the Al and the Ce in the melt.

$$\text{PC} = \frac{\text{Ce (Al)}}{\text{Ce (melt)}} \quad (13)$$

This should be nearly constant for conditions with low Ce concentration.

D. Testing of CEROX Coatings on SnO₂

The first set of experiments performed in this program used SnO₂ substrates for deposition of the CEROX coatings. SnO₂ was selected for evaluation because of ELTECH's extensive experience

with this material. Doped SnO_2 can achieve very high electrical conductivity and low solubility in molten cryolite. Because of this, SnO_2 has long been considered a leading, pure ceramic inert anode candidate. Ten experiments were performed using the SnO_2 substrates. Two variables were considered, the nominal cerium oxide concentration and the current density. Three CeO_2 concentrations were considered, 0.5%, 1.0% and 1.5%. Three current densities were also considered, 0.8, 1.4 and 2.0 A/cm^2 . A full factorial, experimental design was employed with the mid-point, 1.0% CeO_2 and 1.4 A/cm^2 , run in duplicate.

The experiments were performed as described in the Materials and Methods section. Anodic polarization curves were obtained every two hours in order to assess the increase in the iR component of the anode potential. The increase was attributed to the development of the CEROX coating. Following the test, both the bath and metal were analyzed for Ce, Sn, Cu and Sb. In all cases, the Sb levels were below the limits of detection. The coated anodes were also examined by optical and, in some cases, scanning electron microscopy.

1. Coating Structure

Scanning electron micrographs of the CEROX coated SnO_2 substrates obtained under the various experimental conditions are shown in Figures 7 and 8. Clearly, all of the coatings obtained are porous, with the pores filled with cryolite. It can be seen that the coating thickness and the average size of the pores in the coating are highly dependent on the nominal cerium concentration, increasing as the concentration increases. This effect is shown in Figure 7. The

0.8 A/cm²

0.5% CeO₂

1.0% CeO₂

1.5% CeO₂

Figure 7. Scanning Electron Micrographs of CEROX Coatings on SnO₂ at 0.8 A/cm². 0.5, 1.0 and 1.5% CeO₂

0.5% CeO₂

0.8 A/cm²

1.4 A/cm²

2.0 A/cm²

Figure 8. Scanning Electron Micrographs of CEROX Coatings on SnO₂ at 0.5 % CeO₂. 0.8, 1.4 and 2 A/cm²

microstructures shown are from those experiments performed at 0.8 A/cm^2 .

The dependence of the coating thickness on current density is less pronounced. However, it appears that the thickness decreases as the current density increases. This feature is most evident in the series of experiments performed with low Ce levels. Figure 8 shows the cross-sections of the CEROX coated SnO_2 as a function of current density with the nominal cerium oxide level of 0.5%. A summary of the effect of the experimental variables on coating thickness is shown in Table 1.

Although several of the samples were examined by SEM, one sample, prepared at 2.0 A/cm^2 with 1% nominal cerium oxide concentration, was further analyzed by SEM, with elements identified by EDX and WDX. This was performed in order to identify the coating composition and to assess cryolite and cerium penetration into the porous SnO_2 substrate. Four regions were selected for examination. Area 1 was the actual CEROX coating. Areas 2 and 3 were within the SnO_2 substrate, .5 mm and 1 mm, respectively, below the surface of the coating. Area 4 was approximately 8 mm into the substrate. Figures 9 - 13 present the microstructural features. Semi-quantitative EDX and WDX results are presented in Table 2.

Several features are apparent from this study. First, the CEROX coating actually contains low levels of F and should be defined as a cerium fluoride doped cerium oxide rather than pure CeO_2 . Cryolite has penetrated the entire depths of both

Table 1. Effect of Current Density and CeO₂ Concentration on CEROX Coating Thickness

Current Density (A/cm ²)	CeO ₂ conc in the bath (w/o)	Maximum Coating Thickness (μ m)
0.8	1.5	2000
0.8	1.0	1500
0.8	0.5	200
1.4	1.5	2000
1.4	1.0	1300
1.4	0.5	150
2.0	1.5	1600
2.0	1.0	700
2.0	0.5	75

2.0 A/cm² 1% CeO₂

a. 100x

b. 300x

c. Al x-ray map

300x

Figure 9. Detailed Scanning Electron Micrograph of C.FROX Coating on SnO₂ (Area 1)

Area no. 1

a.

1000x

b.

3000x

Figure 10. Detailed Scanning Electron Micrograph of CEROX Coating on SnO_2 (Area 1)

Area no. 2

a.

100x

b.

1000x

Figure 11. Detailed Scanning Electron Micrograph of CEROX Coating on SnO_2 (Area 2)

Area no. 3

a.

100x

b.

1000x

Figure 12. Detailed Scanning Electron Micrograph of CEROX Coating on SnO_2 (Area 3)

Area no. 4

a.

100x

b.

1000x

Figure 13. Detailed Scanning Electron Micrograph of CEROX Coating on SnO_2 (Area 4)

Table 2. Microprobe Analysis of CEROX on SnO₂ Figures 9-13

Area	Fig. No.	Spot Position	Net X-ray Cps		Gross X-ray Counts						
			O	F	Na	Al	Ca	Cu	Sn	Sb	Ce
1	11	A	NA*	NA*	—	—	—	—	454	—	10,172
1	11	B	3,446	124	—	—	—	—	403	—	10,582
1	11	C	3,445	125	—	—	—	—	377	—	10,163
1	11	D	3,489	177	—	—	—	—	385	—	10,273
1	11	E	1,376	0	—	—	—	—	13,316	—	—
1	11	F	1,322	0	—	—	—	—	13,498	—	—
1	11	G	NA*	NA*	3,396	6,416	1,415	—	109	—	—
1	11	H	7,461	1,897	1,864	11,450	927	—	115	—	—
1	11	I	NA	NA	173	1,119	—	—	315	—	7,645
1	11	J	NA	NA	880	15,105	474	—	418	—	—
1	11	K	NA	NA	—	1,827	—	—	10,216	—	239
1	11	L	NA	NA	—	198	—	—	4,391	—	5,505
1	11	M	NA	NA	—	197	—	—	366	—	3,913
2	12	N	4,085	168	209	—	—	—	—	9,224	—
2	12	O	1,337	0	—	—	—	—	13,769	—	—
2	12	P	NA	1,609	2,564	5,641	783	—	233	—	—
3	13	Q	2,964	0	—	—	—	5,721	460	—	—
3	13	R	4,326	162	249	391	—	—	—	10,059	313
3	13	S	1,397	0	—	—	—	—	13,565	—	—
3	13	T	NA	2,387	2,390	5,325	1,134	—	207	—	—
4	14	U	2,994	0	—	—	—	5,503	424	—	—
4	14	V	1,407	0	—	—	—	—	13,213	—	—
4	14	W	NA	2,502	3,569	5,814	446	—	250	—	—

*NA = Not Analyzed

the CEROX coating and the SnO_2 substrate. No Ce is detected in the cryolite within the pores, having been completely precipitated from solution. As in the as-received SnO_2 , CuO and Sb_2O_5 are found dispersed as isolated precipitates within the SnO_2 matrix.

2. Metal Analysis

An indirect measure of the corrosive attack on an anode/anode substrate is the level of impurities in the cryolite and aluminum. In the studies using SnO_2 anodes, the cryolite bath and Al pool were analyzed for Sn, Cu, and Sb since Cu and Sb are the major metallic dopants of this SnO_2 . In all cases, Sb levels were below the detection limits of analysis and are, therefore, not presented in this report. Cu and Sn levels in the cryolite melt were also found to be quite low. In most experiments, these were also below the limits of detection. The low levels of these impurities in cryolite are due to the strong electrochemical driving force for these to be cathodically deposited in the Al pool.

The Sn and Cu levels in the aluminum are shown in Table 3. Also shown in the table are the amounts of Al produced under each of the conditions. In general, the laboratory cell operated at approximately 50% current efficiency. From the tin analyses shown in the table, it can be seen that the Sn levels are reduced by an increase in the Ce in the bath. The dependence of the protection on the initial cerium level is best demonstrated by the data obtained at 0.8 A/cm^2 , and is shown in Figure 14. It can be

Table 3. Tin and Copper Levels in Aluminum Pool as a Function of Current Density and CeO₂ Bath Levels

<u>Run #</u>	<u>Nominal Ce (w/o)</u>	<u>Current Density (A/cm²)</u>	<u>Sn/Al (w/o)</u>	<u>Cu/Al (w/o)</u>	<u>Al Produced (g)</u>
1	0.5	0.8	.170	.200	3.0
2	0.5	1.4	.340	.320	6.7
3	0.5	2.0	.042	.076	9.0
4	1.0	0.8	.040	.140	2.8
5	1.0	1.4	.570	.190	7.0
6	1.0	1.4	.190	.260	7.1
7	1.0	2.0	1.00	.220	8.7
8	1.5	0.8	.011	.180	3.2
9	1.5	1.4	.110	.120	6.3
10	1.5	2.0	.870	.170	0.8

Figure 14. Percent Tin in Aluminum as a Function of CeO_2 Concentration in Bath. 0.8 A/cm²

seen in the figure that the Sn levels in the aluminum pool are reduced by more than an order of magnitude when increasing the cerium level from 0.5% to 1.5%. This is reflective of the development of a protective CEROX layer.

It is also evident that the current density has a deleterious effect on this protection. The effect of current density is best demonstrated by the experiments performed at 1.5% CeO₂. The Sn levels obtained from these tests are shown in Figure 15. As shown in the figure, the current density can influence the Sn levels by nearly two orders of magnitude.

Statistical analysis of the data in Table 3 yielded as the best fit model the following equation describing the percent Sn, as a function of the nominal Ce level and the current density (CD):

$$\% \text{ Sn} = .457 + .65 \text{ Ce} - 1.0 \text{ CD} + .82 \text{ Ce*CD}$$

$$r^2 = .915$$

Statistically, the dominant factor which increases the Sn levels is the cross product term Ce*CD, not the current density alone. The dominance of the interactive term Ce*CD in the best fit model implies the effect of the current density is to diminish the protection afforded by the CeO₂ layer.

Because the SnO₂ material is doped with copper, the concentration of copper in the aluminum can also serve as a measure of substrate corrosion. Results of the copper analyses as a function of Ce level and current density are also shown in Table 1. It is interesting to note that in many cases the Cu levels are of the same order of magnitude as the Sn levels. In all cases, the Cu/Sn concentration ratios were more than a factor of 10 greater

Figure 15. Percent Tin in aluminum as a Function of Current Density.
1.5% CeO_2 Concentration

than that in the as-received tin oxide. This suggests a preferential dissolution of the Cu phase from the SnO₂ matrix.

As was the case with the Sn data, the Cu in the Al decreased with increasing Ce concentration and increased with increasing current density. The best fit model, with an r^2 value of .877, is described by:

$$\% \text{ Cu} = .08 - .15 \text{ Ce} + .32 \text{ CD} - .18 \text{ Ce} \cdot \text{CD}$$

Just as in the analysis of the Sn data, it is concluded that effect of the current density is to diminish the protective nature of the CEROX coating.

Because the aluminum was not analyzed as a function of time, it is impossible to establish a wear rate of the tin oxide, coated or uncoated. As will be shown in a later section, it is possible that a fraction of the tin could be introduced during the cell startup. Therefore, projecting a wear rate based on one data point may greatly misrepresent the true steady-state wear. However, it seems likely that the results obtained in these studies would be of value in predicting cerium oxide concentrations and current densities which might provide the maximum substrate protection. However, further experiments, performed for longer time with periodic metal analyses, would be required to assess the magnitude of the decrease in substrate wear rate in the presence of a CEROX coating.

3. Cerium Partitioning

Chemical analysis of the Ce in Al and cryolite in our experiments with SnO₂ anodes allows us to calculate the Ce partition coefficients. Results are shown in Table 4. In these experiments, the following conclusions can be drawn:

Table 4. Partition Coefficient for Cerium in SnO₂ Trials

<u>SnO₂ T-1185 Anodes</u>					
<u>Run #</u>	<u>Nominal Ce (w/o)</u>	<u>Current Density (A/cm²)</u>	<u>Ce (Al) (w/o)</u>	<u>Ce (Melt) (w/o)</u>	<u>Partition Coefficient</u>
1	0.5	0.8	2.20	0.26	8.5
2	0.5	1.4	2.40	0.29	8.3
3	0.5	2.0	1.60	0.27	5.9
4	1.0	0.8	2.10	0.26	8.1
5	1.0	1.4	2.30	0.32	7.2
6	1.0	1.4	3.70	0.31	11.9
7	1.0	2.0	2.70	0.32	8.4
8	1.5	0.8	3.40	0.44	7.7
9	1.5	1.4	3.40	0.36	9.4
10	1.5	2.0	3.20	0.53	6.0

Avg. PC = 8.1 $\pm$ 1.7

- a. Ce levels in the aluminum pool generally ranged from 2 - 3.5%. For a commercial practice, a Ce recovery process would be required. The recovered cerium would then be recycled to the cell.
- b. The partition coefficient is nearly constant, averaging approximately 8.1 for all of the experiments conducted.
- c. The cerium content in both the cryolite and Al increases with the nominal CeO_2 added.
- d. At a given value of the nominal CeO_2 , the Ce in both the Al and melt is insensitive to current density.

It should be noted that since the partitioning of cerium involves the equilibrium between CeF_3 , Al, AlF_3 and Ce, a reduction in the bath ratio, i.e., an increase in the AlF_3 activity, should reduce the partition coefficient. However, it cannot be concluded that this would reduce the Ce level in the Al. A decrease in the bath ratio could increase the steady-state CeF_3 concentration in the melt by inhibiting CeO_2 deposition at the anode.

4. CEROX Coating Resistance

In all of the experimental runs using the SnO_2 T-1185 anodes, polarization curves were obtained at 2 hour intervals. The iR free anode potentials were also obtained by use of current interrupt techniques. The iR free potentials were found to be nearly constant with time and were reproducible with all the runs. A representative iR free polarization curve is shown in Figure 16. It can be noted that the curve

Figure 16. IR-free Anode Potential vs Log Current Density

has two straight segments with slopes of approximately 0.06 and 0.14 ohm-cm². This can be interpreted as evidence of a two step discharge reaction. The fact that the curves do not vary with time suggests that the O₂ overpotential is insensitive to the development of the CeO₂ coating.

Although the iR free anode potentials did not vary with time, the uncorrected anode potentials demonstrated a significant time dependence during electrolysis. In all cases with CeO₂ in the bath, anode potentials rose during the first two hours of electrolysis. The magnitude of the rise appears to be dependent on both the concentration of the CeO₂ in the bath and the current density.

After two hours, the anode potentials were found to decrease, generally reaching a plateau within 6 hours. In nearly all cases, the anode potentials were higher at the end of a run than at the beginning of the run. This increase in anode potential is attributed to the development of the CeO₂ coating which adds a resistive component to the uncorrected anode potential. This resistance term could be due to the electrical resistivity of the CEROX layer. Alternatively, it could be due to an increase in the bath resistance due to a change in bubble distribution or entrapped bubbles at the surface. Further fundamental studies would be required to distinguish these effects.

The electrical resistance of the CeO₂ coatings was estimated from the change in the iR component of the anode potentials, measured at the beginning and the end of each

experimental run. These are summarized in Table 5. The maximum resistance measured was 0.44 ohm-cm^2 , obtained at 0.8 A/cm^2 and 1.5% CeO_2 in the bath. At the other extreme, there was no measurable increase in resistance at 0.5% CeO_2 at 1.4 and 2.0 A/cm^2 .

As can be seen in the data, increasing the CeO_2 in the bath increases the resistance attributed to the development of the coating. This is, of course, the expected result since the CeO_2 level is the major factor affecting the coating thickness. Increasing current density decreases the change in resistance. This is probably due to increased coating porosity and decrease in thickness of coatings obtained at high current.

It should be noted that the factors which decrease the coating resistance also decrease the degree of protection afforded the substrate by the coating. It appears that the most protective coating will be that with the highest resistance.

E. Cermet Characterization

The copper containing nickel ferrite materials used in our studies were supplied by Pacific Northwest Laboratories. These were actually prepared in two production runs, run 48 and 51. The raw materials used in both runs were identical. Because the materials were prepared in two lots, samples from both lots were selected for characterization by chemical analysis, X-ray diffraction and scanning electron microscopy. The results presented below indicate that the materials from both lots were

Table 5. CEROX Coating Resistance as a Function of Current Density and CeO_2 Bath Concentration

<u>Run #</u>	<u>Nominal Ce (w/o)</u>	<u>Current Density (A/cm²)</u>	<u>Calculated Resistance⁺ (ohm-cm²)</u>
1	0.5	0.8	.175
2	0.5	1.4	*
3	0.5	2.0	*
4	1.0	0.8	.304
5	1.0	1.4	.248
6	1.0	1.4	.120
7	1.0	2.0	.358
8	1.5	0.8	.440
9	1.5	1.4	.339
10	1.5	2.0	.135

* Zero or negative resistance change.

⁺ Multiplying this resistance by current density (A/cm²) yields the voltage drop associated with the coating.

identical, as assessed by these analytical methods.

1. Chemical Analysis

Samples were taken from three randomly selected cermet for chemical analysis. As was discussed in the Materials and Methods section, the cermet samples were dissolved by fusion in a molten Na_2O flux and the elements analyzed by inductively coupled plasma spectroscopy. The results of these analyses are shown below:

<u>Sample #</u>	<u>%Cu</u>	<u>%Fe</u>	<u>%Ni</u>
48-3	17.5	29.0	32.9
48-11	18.6	28.1	32.0
51-5	18.6	28.5	32.5
Avg.	18.2	28.5	32.5

The targeted composition of the cermet 5324/17 Cu is 17% Cu, 28.04% Fe and 33.72% Ni. Based on the results from the analyses, it is apparent that the cermet was slightly Cu rich, implying a higher than targeted level of metallic phase. In addition, the ratio of %Fe/%Ni is also slightly high. Again this indicates that the ferrite powder was slightly off target.

2. X-ray Diffraction

The same three samples were analyzed by x-ray diffraction for phase composition and phase purity. In all three samples, two major crystalline phases were detected. Within the Cu, Fe, Ni and O systems these two phases could be identified as:

1. NiFe_2O_4 and/or CuFe_2O_4
2. Cu and/or Cu-Ni and/or FeNi

Unfortunately, it was impossible to distinguish the various compounds because of the similarity of the powder

diffraction pattern data. More information concerning phase composition was obtained from SEM and EDX. This data is discussed below.

3. Scanning Electron Microscopy

Samples were taken from three randomly selected cermets, 48-2, 48-7 and 51-5, for examination by SEM and EDX/WDX microprobe analysis to identify the phases present. The polished metallographic mounts were carbon coated for this analysis.

All elements from Na through U were analyzed by EDX. In all three samples, only Cu, Fe and Ni were detected. WDX analysis was used to determine B, C, N and O.

All of the samples appeared to be quite similar by SEM. Representative micrographs are presented in Figure 17. Three distinct phases are apparent in the figure. Spots A and B correspond to a metallic phase. The semiquantitative EXD results indicate that this phase consists of approximately 80% Cu and 20% Ni. No oxygen was detected by WDX. Spots C and D are a ferrite phase, rich in Ni. The Ni levels are approximately three times the Fe levels in this phase. Oxygen is clearly detected by WDX. Finally, spots E and F also are an oxygen containing phase, rich in Fe relative to Ni. Fe levels are approximately 4 times those of Ni.

Based on the EDX/WDX analyses, it appears that the cermets are actually composed of three phases; two ceramic phases and one metallic phase. The ceramic phases are distinguished by the relative Fe and Ni concentrations. The metallic phase appears to be an alloy of Cu and Ni.

Figure 17. Scanning Electron Micrograph as As-Received PNL 5324/ 17% Cu Cermet

4. Thermal Properties

One of the copper containing nickel ferrites, 48-1 was sacrificed in order to obtain specimens for thermal analysis. All of the thermal studies were performed at the Thermal-Physical Laboratory at Purdue University.

The specific heat of the cermet as a function of temperature is summarized in Table 6 and plotted in Figure 18. There is an inflection near 200°C and a peak near 585°C. The peak was attributed to the Curie transformation since the material remains magnetic above 200°C.

Thermal diffusivity results are also shown in Table 6 and are plotted in Figure 19. The curve exhibits a strong inflection near 200°C and a rally near 600°C. The latter corresponds to the peak in the specific heat. At 1000°C, the thermal diffusivity was measured at 0.0131 cm²/sec. From the specific heat and thermal diffusivity results, thermal conductivity values have been calculated. As shown in Figure 20, thermal conductivity exhibit several maxima and minima. At 1000°C, the thermal conductivity is calculated to be .066 W/cm/K.

Thermal expansion results are shown in Table 7 and are plotted in Figure 21 (thermal expansion) and Figure 22 (mean thermal expansion coefficient). The mean thermal expansion coefficient is somewhat non-linear with temperature.

Table 6. Thermal Conductivity of PNL Cermet as a Function of Temperature

<u>Temp.</u> <u>(C)</u>	<u>Density</u> <u>(gm cm⁻³)</u>	<u>Specific Heat</u> <u>(W s gm⁻¹K⁻¹)</u>	<u>Diffusivity</u> <u>(cm²sec⁻¹)</u>	<u>Conductivity</u> <u>(W cm⁻¹K⁻¹)</u>
22.0	5.992	0.5670	0.02350	0.07984
100.0	5.992	0.6490	0.02160	0.08400
200.0	5.992	0.7230	0.01730	0.07495
300.0	5.992	0.7220	0.01540	0.06662
400.0	5.992	0.7450	0.01530	0.06830
500.0	5.992	0.7950	0.01480	0.07050
600.0	5.992	0.8060	0.01360	0.06568
700.0	5.992	0.7380	0.01440	0.06368
800.0	5.992	0.7720	0.01400	0.06476
900.0	5.992	0.8100	0.01300	0.06310
1000.0	5.992	0.8420	0.01310	0.06609

Figure 18. Specific Heat of Cermet as a Function of Temperature

Figure 19. Temperature Dependence of Cermet Thermal Diffusivity

Figure 20. Temperature Dependence of Cermet Thermal Conductivity

Table 7. Thermal Expansion of PNL Cermet

<u>TEMP.</u> <u>(C)</u>	<u>L/Lo</u> <u>(in/in)</u>	<u>MEAN*</u> <u>(C⁻¹x10⁶)</u>
97.0	0.000796	11.2
147.0	0.001438	11.9
197.0	0.002121	12.4
247.0	0.002787	12.6
297.0	0.003364	12.4
347.0	0.004149	12.9
397.0	0.004845	13.1
447.0	0.005612	13.3
497.0	0.006410	13.6
547.0	0.007243	13.9
597.0	0.007930	13.9
647.0	0.008578	13.8
697.0	0.009249	13.8
747.0	0.009809	13.6
797.0	0.010450	13.6
847.0	0.011260	13.7
897.0	0.012050	13.8
947.0	0.012950	14.1
997.0	0.013950	14.4

*Expansion/(T-24)

Figure 21. Thermal Expansion of PNL Cermet

Figure 22. Temperature Dependence of the Mean Thermal Expansion Coefficient of the PNL Cermet

5. Electrical Resistivity

The electrical resistivity of one cermet, 48-1, was determined as a function of temperature. Results of this determination are shown in Figure 23 with resistivity plotted as a function of inverse temperature. At 1000°C, the resistivity was .039 ohm-cm. This was slightly higher than that reported by ALCOA for a cermet of this composition. The room temperature resistivity was .76 ohm-cm.

Figure 23. Temperature Dependence of the Electrical Resistivity of the PNL Cermet

F. Cermet Testing in Cerium Free Bath

Prior to the testing of CEROX coated cermets, several runs were made in the laboratory Hall cell of the cermet using a cerium free cryolite bath. These experiments served as controls for the CEROX experiments. All of the controls were run using an electrolyte defined in the Materials and Methods section: ratio of 1.35 with 8% Al_2O_3 and 5% CaF_2 . Three varying current densities: 0.8, 1.4 and 2.0 A/cm^2 . In addition, one time course experiment was performed at 1.4 A/cm^2 . The time course experiment actually consisted of 5 runs of 2, 4, 6, 8 and 10 hour durations. After each run, the metal and bath were recovered and analyzed for Fe, Cu and Ni. In addition, the anodes from each run were sectioned and examined microstructurally.

1. Effect of Current Density

Table 8 shows the Fe, Cu and Ni analyses of the aluminum pool from tests conducted with the copper containing nickel ferrite in cerium-free bath at different current densities. The data presented for the current density of 1.4 A/cm^2 is really an average of two results.

Table 8. Metal Analysis from Cermet Runs in Cerium-Free Bath

<u>Experiment Number</u>	<u>Current Density (A/cm^2)</u>	<u>Fe (ppm)</u>	<u>Cu (ppm)</u>	<u>Ni (ppm)</u>
33	0.8	6100	2000	130
37-30	1.4	6800	2300	1400
35	2.0	7600	2400	1100

The most striking result here is that the Fe levels are much higher than the Ni levels, despite the fact that in the cermet the Fe and Ni levels are nearly the same. This

indicates that within the time frame of the experiments, Fe is leached, preferentially from the cermet. This effect was also observed by workers at ALCOA, who later found that the % Fe/% Ni ratio in the aluminum approached the stoichiometric ratio of the cermet as the time of the test increased. It was proposed by Alcoa, that as the Fe was leached preferentially, the surface of the cermet became Ni rich. Eventually the Fe recedes to the point that the Fe and Ni are dissolved at rates proportional to the stoichiometric levels. (5)

A preferential leaching of Fe is not consistent with microstructural analysis of the tested cermet. As shown in Figure 24, microstructurally there is no evidence of a reaction zone at the surface. The discrepancy can be rationalized in one of two ways.

- a) The reaction zone on the cermet spalls off during cooling after the test.
- b) The cermet corrodes uniformly. However, the rate at which impurities are introduced into the Al is cathode limited. In this case, higher Ni levels would be expected in the bath. This was not observed in our studies.

There does appear to be a relationship between impurity levels and current density. As shown in Figure 25, the Fe levels increase with current density. Since the amount of Al recovered is much higher at higher current densities, the actual wear of the anode increases much more significantly with current density than is shown in the figure.

1.4 A/cm² : No Ce O₂ addition

Figure 24. Scanning Electron Micrograph of Cermet Tested in Cerium-Free Bath. 1.4 A/cm²

Figure 25. Percent Fe in Aluminum as a Function of Current Density.
Cerium-Free Bath

2. Time Course Experiment

The one time course study performed in Ce-free bath was conducted at a current density of 1.4 A/cm^2 . This represented the midpoint of the current densities examined.

Five experiments (all run in duplicate) were run at 2, 4, 6, 8 and 10 hours. Analysis of the recovered aluminum for iron is plotted as a function of time in Figure 26. The least squares fit of the Fe analysis data has the form:

$$\% \text{ Fe} = 0.5697 + 0.016 \times \text{time (hours)}$$

This suggests that anode wear does occur since the Fe levels increase with time. However, it also indicates that most of the Fe impurities introduced to the cell occur during start-up of the test.

In order to examine the effect of start-up on Fe levels, a subsequent experiment was performed in which a cermet anode was suspended above the cryolite as the cell was brought up to temperature. This would be our normal start-up procedure. Once the melt had reached temperature, the heat was shut off. The metal from this test, having never been polarized was found to contain .59 % Fe. This result is consistent with our time course trials, and suggests a very rapid corrosion of the ferrite. This same effect was reported by ALCOA in their laboratory tests (see, for example, run R64M in ALCOA's final report DOE/CS/40158-20) (5). The ALCOA tests also show a rapid onset of Fe in the Al followed by a much slower

Figure 26. Percent Fe in Al as a Function of Time. Cerium-Free Time Course Experiment

accumulation of impurities. The absolute levels in the ALCOA tests are lower than in our results due to the fact that a much larger Al pool was used in their tests. In other words, the fixed amount of impurities were dissolved in a larger pool. ALCOA explained this by hypothesising a rapid initial corrosion of the ferrite until the bath is saturated with the ferrite components. After the bath is saturated, the anode dissolves at a constant, much lower rate.

In our time course study, the copper levels, although lower than the Fe levels, show the same behavior; a rapid onset followed by a slow accumulation of impurities. The Ni levels were generally too low to detect an increase with time.

The wear of the anode with time is best assessed by examining the total amount of Fe recovered from the aluminum (the product of the % Fe and the mass of aluminum) as a function of time. This is shown in Figure 27. Here the levels are definitely increasing and the effect of the initial Fe (at zero time) is less significant.

Based on the slope of the line in Figure 27, a wear rate of the copper containing nickel ferrite can be calculated. Assuming a 95% current efficiency in commercial practice, the aluminum pool would have a projected iron level of 0.95%. This is higher than that extrapolated from ALCOA's screening tests. However, our test was performed at a higher current density (1.4 A/cm^2) than any of ALCOA's tests. The data shown in this section clearly indicates that the cermet wear rate increases with current density.

Figure 27. Total Fe in Al as Function of Time. Cerium Free Time Course Experiment

It must be emphasized that caution must be exercised in projecting wear rates based on the results of a ten hour test, since the kinetics of the experimental system have not achieved steady state. This is most evidenced by the fact that the impurities in the Al are not present in their stoichiometric ratios. In order to project accurate wear rates, it is necessary to run tests of sufficient duration to establish steady state operation.

Figure 28 shows the adjusted weight percent of iron deposited in the electrolytic aluminum as a function of time. The amount of deposited iron is determined by subtracting the amount of iron dissolved in the aluminum at the time of cell startup (the intercept of Figure 27). The adjusted weight of deposited iron is then divided by the theoretical amount of aluminum produced during operation. The plot indicates that the aluminum produced after initial startup has an iron concentration of approximately 0.90 weight percent.

Figure 28. Adjusted Weight Percent of Iron Deposited in Electrowon Aluminum. Cerium-Free Time Course Experiment

G. Testing of Cermet in Cerium Containing Bath

Ten 10-hour experiments were performed in which CEROX coatings were deposited on the PNL cermets at varying current density and nominal CeO_2 additions. As in the previous study with SnO_2 substrates, a full factorial experimental design was employed considering current density and nominal cerium level as independent variables. Again, the current densities examined were 0.8, 1.4 and 2.0 A/cm^2 and the CeO_2 levels were 0.5%, 1.0% and 1.5%. The mid-point experiment, 1.0% CeO_2 and 1.4 A/cm^2 , was performed in duplicate.

The experiments were performed as described in the Materials and Methods section. Again polarization curves were obtained every two hours to assess the coating resistance. Following the test, the bath and metal were analyzed for Ce, Fe, Cu and Ni. The Ce levels were used to calculate partition coefficients and the Fe, Cu and Ni levels used to assess anode wear.

1. CEROX Coating

Scanning electron micrographs of the CEROX coated cermets substrates obtained under the various experimental conditions are shown in Figures 29-31. As was the case with SnO_2 substrates, all of the coatings obtained are porous with the pores filled with cryolite. The trends seen with the SnO_2 substrates are also seen with cermets. In this regard, the deposition of CEROX coatings appears insensitive to the chemical nature of the substrate.

It can be seen that the coating thickness and the average size of the pores in the coating are highly dependent on the nominal

0.5% CeO_2

Figure 29. Scanning Electron Micrographs of CEROX Coated Cermet as a Function of CeO_2 Bath Concentration. 0.8 A/cm²

1% CeO_2

0.8 A/cm^2 25KV X10 4614 1000.0U RIC

1.4 A/cm^2 25KV X10 4602 1000.0U RIC

2.0 A/cm^2 25KV X10 4620 1000.0U RIC

Figure 30. Scanning Electron Micrographs of CEROX Coated Cermet as a Function of CeO_2 Bath Concentration. 1.4 A/cm^2

1.5% CeO₂

0.8 A/cm²

1.4 A/cm²

2.0 A/cm²

Figure 31. Scanning Electron Micrographs of CEROX Coated Cermet as a Function of CeO₂ Bath Concentration. 2.0 A/cm²

cerium concentration, increasing as the concentration increases. The dependence of the coating thickness on current density is less pronounced, although, it appears that the thickness decreases as the current density increase.

2. Cerium Partitioning

As in our previous studies with SnO_2 anodes, Ce analyses of the aluminum and cryolite melt were performed in order to establish a metal-melt partition coefficient. Results of these analyses are shown in Table 9, along with the calculated partition coefficients. In general, the percent Ce in the Al ranged from 1.5% to 2.5%. Although the percent Ce in the metal may increase with the nominal cerium added, the partition coefficients appeared to be insensitive to cerium addition or current density. The higher Ce levels in the Al, observed with an increase in the nominal cerium level, are due to higher Ce bath concentrations.

The average partition value was found to be 5.92 ± 1.87 . This value is statistically different from that determined in our SnO_2 studies (8.1). At this point, it is unclear what role the nature of the anode could have on the partitioning of the cerium in the cell.

3. Coating Resistance

In all of the experiments, the change in the iR component of the anode potential from the zero time value was used to assess the resistance of the coating. This resistance may actually be due to the electrical resistance of the coating or possibly could be attributable to gas bubble effects. Unfortunately, with the present experiments, it is impossible to distinguish these

Table 9. Cerium Partition Coefficients for Cermet Trials

<u>Current Density</u>	<u>Nominal Cerium</u>	<u>%Ce/Al</u>	<u>%Ce/Bath</u>	<u>P.C.</u>
0.8	0.5	1.4	.24	5.83
1.4	0.5	2.1	.26	8.08
2.0	0.5	1.7	.26	6.54
0.8	1.0	1.9	.30	6.33
1.4	1.0	1.5	.23	6.52
1.4	1.0	2.0	.23	8.70
2.0	1.0	2.2	.57	3.86
0.8	1.5	2.1	.94	2.23
1.4	1.5	2.1	.42	5.00
2.0	1.5	2.5	.41	6.10

Ave. = 5.92 ± 1.87

effects. As was seen in the SnO_2 studies, in nearly all cases, the increase in resistance peaked at two hours, and decreased to a plateau by 6 hours.

The anode coating resistances obtained from each 10 hour experiment are shown in Table 10. As can be seen in the data, decreasing the CeO_2 in the bath decreases the magnitude of the coating resistance. This is, of course, the expected result since the nominal CeO_2 level is the major factor affecting the coating thickness. Increasing the current density decreases the coating resistance. This is likely due to increased coating porosity obtained at high current.

4. Metal Purity

In all of the ten experiments, the iron and copper levels in the aluminum were less than those found in control experiments (with no cerium in the bath). Increasing the cerium levels in the bath decreased the amount of impurities introduced into the aluminum. Figure 32 shows the data obtained at 0.8 A/cm^2 . Both the Fe and Cu levels decrease with increasing Ce levels. The same trend is obtained at higher currents (1.4 A/cm^2 and 2.0 A/cm^2). These data are shown in Figures 33 and 34.

It should be noted that the Fe and Cu levels obtained are, in some cases, lower than those obtained at zero time in the experiments performed with no cerium. This is believed to be a consequence of the fact that as the experiment progresses, the size of the Al pool is growing. Because of this, impurities which are present initially are diluted. In fact, the Fe levels obtained in the experiment conducted at 0.8 A/cm^2 with 1.5% CeO_2

Table 10. CEROX Coating Resistances Determined in Cermet Trials

Current Density <u>A/cm²</u>	Nominal Cerium <u>%</u>	Resistance <u>OHM-cm²</u>
0.8	0.5	.203
1.4	0.5	0
2.0	0.5	0
0.8	1.0	.408
1.4	1.0	.367
2.0	1.0	0
0.8	1.5	.698
1.4	1.5	.290
2.0	1.5	.159

Figure 32. Effect of Nominal CeO₂ Bath Concentration of Fe and Cu Levels in Aluminum. 0.8 A/cm²

Figure 33. Effect of Nominal CeO_2 Bath Concentration of Fe and Cu Levels in Aluminum. 1.4 A/cm^2

Figure 34. Effect of Nominal CeO₂ Bath Concentration of Fe and Cu Levels in Aluminum. 2.0 A/cm²

are well predicted by assuming a fast initial corrosion (equal to the zero time experiments with no CeO_2 in the bath) and no subsequent corrosion.

In Figure 35, the total Fe levels found in the recovered Al pool are plotted against current density for the experiments performed with 1.5% CeO_2 added to the bath. These are calculated based on the Al recovered from each test. A minimum value was obtained at 0.8 A/cm^2 . The impurity levels increase at 1.4 A/cm^2 and greatly increase in the 2.0 A/cm^2 experiment. This should indicate that at the higher current densities, the cermet is corroding beyond the initial time. Some protection is afforded by the coatings, as evidenced by the decrease in Fe levels with respect to the control values. However, the CEROX coating is only partially effective in preventing attack on the cermet at high current densities.

5. Cermet Microscopy

As was mentioned in section G-1, a reaction layer in the cermet beneath the CEROX coating appeared to develop during testing. This layer was not seen in all cases. At low current density and high cerium levels no reaction layer was observed. Of course, under these conditions the Fe, Cu and Ni impurities in the aluminum were at a minimum. However, in experiments in which corrosion is higher (as assessed by the metal purity), the reaction layer was observed. Since the development of the reaction layer appears to be related to the cermet corrosion, further characterization of the layer by SEM with x-ray mapping was performed.

Figure 35. Total Fe as Recovered Al as a Function of Current Density

The sample selected for further study was that prepared at the mid-point of the experimental design, 1.4 A/cm^2 , and a cerium oxide bath concentration of 1.0%. These were also the conditions selected for the time course study, discussed in a later section. Figure 36 shows the backscattered SEM micrograph of the transverse section of the coated anode substrate. Two reaction layers are observed. The first is only 100 microns in thickness and the second extends to a depth of 1 mm.

Also shown in Figure 37 are x-ray maps for Fe, Cu and Ni. It is apparent that the Cu is depleted from the thin reaction layer. However, a high concentration of Cu is found directly beneath the CEROX coating. It appears that the Cu is diffusing out of the substrate and is blocked by the CEROX coating. In the thicker reaction layer, the Cu is still present but appears to be redistributed. The copper could be oxidized; however, this cannot be determined without further work. More interesting is the fact that the major reaction layer appears to be Fe depleted when compared to as received material. On the other hand, the Ni distribution is unchanged. This suggests a preferential dissolution of Fe. This is consistent with the results from our bath analyses.

In conclusion, it appears that beneath the CEROX layer, Fe is preferentially attacked, leaving a Ni rich matrix. Copper is also attacked near the surface. However, diffusion out of the substrate appears to be blocked by the CEROX coating. This blocking effect is microstructural evidence of the protective nature of the coating.

Backscattered SEM

1% CeO₂ : 1.4 A/cm²

Figure 36. Backscattered SEM of CEROX Coated Cermet with Reaction Layer. 1.4 A/cm²; 1.0% CeO₂ in Bath

1.4 A/cm²
1.0% CeO₂

Cu map

Fe map

Ni map

Figure 37. X-Ray Maps of Reaction Layer in CEROX Coated Cermet

As will be seen in a later section, under preferred conditions, this reaction layer is not observed. In the absence of the reaction layer, corrosion of the cermet cannot be detected.

H. Time Course Tests of CEROX on Cermet

In studying the anodic deposition of CeO_2 on the PNL cermet, two time course experiments were performed. In these experiments, the cryolite and aluminum were analyzed chemically and the anode coatings examined microstructurally after 2, 4, 6, 8 and 10 hours. The first experiment was performed at 1.4 A/cm^2 and 1% CeO_2 in the bath. This represented the center point condition of our experimental design. The second experiment was performed at 0.8 A/cm^2 with 1.5% CeO_2 in the bath. Previous work had established that within our experimental matrix, these conditions showed the minimum cermet corrosion, as assessed by metal purity. Comparison of the results from these two time course experiments dramatically demonstrates the increased protection obtained from coatings obtained at lower current density and higher CeO_2 levels.

1. Midpoint Conditions

At 1.4 A/cm^2 and 1% CeO_2 , the percent cerium in both the aluminum pool and the cryolite melt decreased with time. This is shown in Figure 38. The fact that both percentages would change together is not surprising, and is reflective of a constant partition coefficient.

In Figure 39, the total amount of cerium present in the aluminum and bath is plotted as a function of time. Here the amount of cerium in the aluminum remains essentially constant. The percent decrease seen in Figure 37 would appear to be the result of a constant amount of cerium present in an aluminum pool

Figure 38. Percent Cerium in Bath and Aluminum as a Function of Time.
1.4 A/cm²; 1.0% CeO₂ Bath Concentration

Figure 39. Total Weight of Cerium in Bath and Aluminum as a Function of Time. 1.4 A/cm²; 1.0% CeO₂ Bath Concentration

which is growing because of electrolysis. Although the cerium level in the cathode pool is nearly constant, the cerium in the bath is decreasing throughout the ten hour experiment. By mass balance considerations, this implies that the CeO_2 coating continues to develop within the time frame of the experiment. The calculated amount of Ce at the anode is also shown in Figure 38. It is important to recognize that since the coating is developing throughout the experiment, our experimental system does not reach steady state. Therefore, one must exercise caution when applying steady state kinetics to calculate corrosion rates of the cermet.

The percent iron found in the Al cathode is shown in Figure 40 as a function of time. Also shown is the weight of the Al as a function of time. The Fe analysis curve shown is very similar to that obtained in the control time course experiment (1.4 A/cm^2 ; no CeO_2). A very rapid increase in the iron level is observed with the first two hours and this is followed by a much lower rate of increase. The intercept of the line is nearly identical to that obtained in the cerium-free experiment. This is expected since the CEROX coating develops during the test and is not present at start-up.

The total iron level in the Al was calculated from the percentages and the weight of aluminum recovered. This is also shown to increase with time (Figure 41), indicating a continuing attack on the cermet. From the slope of the line, a projected anode wear rate was calculated. Assuming a 95% current efficiency, under these experimental conditions, the aluminum pool would contain 0.57% iron. This figure represents approximately a one third reduction in the anode wear rate

Figure 40. Weight Percent Fe in Aluminum Pool as a Function of Time.
1.4 A/cm²; 1.0% CeO₂ Bath Concentration

Figure 41. Total Weight of Fe in Aluminum as a Function of Time. 1.4 A/cm²; 1.0% CeO₂ Bath Concentration

compared to the control experiment in Ce-free bath. In order to visualize the protection afforded, the cermet substrate by the cerium oxide coating, Figure 41 is directly compared to the control run results. This is shown in Figure 42. The decrease in slope observed with Ce in the bath is apparent.

Just as in the control experiment, a steady state condition has not been achieved in this 10 hour time course experiment. Therefore, one must exercise caution when calculating steady state wear rates. Figure 43 shows the adjusted weight percent of iron deposited in the electrowon aluminum as a function of time. The plot indicates that the aluminum produced after initial startup has an iron concentration of approximately 0.55 weight percent.

As was shown in section G-5, a reaction layer was observed in the cermet below the surface of the coating in the experiment performed at 1.4 A/cm^2 and 1.0% Ce. This reaction zone appeared to be the result of preferential leaching of Fe from the ferrite matrix and by a redistribution of the Cu. The development of the reaction zone was also apparent in this experiment since the experimental conditions were the same.

Figure 44 shows SEM micrographs of the anode substrates obtained from this time course study. The samples shown represent testing of 2, 4, 6 and 8 hours. It is evident that not only does a reaction layer occur, but that the width of the layer increases with time. This observation is consistent with the metal analysis data indicating that corrosion of the

Figure 42. Comparison of Time Course Experiments Performed at 1.4 A/cm². No Cerium and 1.0% CeO₂

Figure 43. Adjusted Weight Percent of Iron Deposited in Electrowon Aluminum. 1.4 A/cm²; 1.0% CeO₂ Bath Concentration

1.0% CeO_2 : 1.4 A/cm²

Figure 44. Scanning Electron Micrographs of CEROX Coated Cermets as a Function of Time with Reaction Layer. 1.4 A/cm²; 1.0% CeO_2

substrate continues with time. The preferential depletion of Fe is also consistent with the high Fe levels found in the metal.

It is not clear how the cermet would perform beyond 10 hours. It is possible that the reaction layer would continue to grow with time. However, it could be that a time would be reached in which cermet corrosion would slow. To resolve this issue, further testing would be required for longer duration.

Based only on the data available, it must be concluded that under these conditions, chemical attack on the cermet does occur. This attack is manifested by the development of a reaction layer in the cermet which grows with time. Based on metal analyses, the rate of cermet corrosion is less than that of the cermet tested at the same current in the absence of cerium. The cerium oxide coating inhibits attack on the substrate, but does not eliminate it under these non-optimum conditions.

2. Preferred Conditions

The results from the time course experiment performed at 0.8 A/cm² and 1.5% CeO₂ are markedly different from those obtained at 1.4 A/cm² and 1% CeO₂. The coating appears to develop faster in the second experiment. More importantly, the attack on the cermet is significantly reduced, to the point that a corrosion rate cannot be determined.

Figure 45 shows the percent cerium found in both the cryolite and the aluminum as a function of time. There is a general decrease in the cerium level in the aluminum, but the cerium content of the bath remains nearly constant. The data is replotted in Figure 46, showing the total amount of cerium in the

Figure 45. Percent Cerium in Bath and Aluminum as a Function of Time.
0.8 A/cm²; 1.5% CeO₂ Bath Concentration

Figure 46. Total Weight of Cerium in Bath and Aluminum as a Function of Time. 0.8 A/cm²; 1.5% CeO₂ Bath Concentration

aluminum and bath, which of course takes into account the amount of aluminum produced during electrolysis. In this case, the amount of cerium in both the bath and cathode pool remain nearly constant. Therefore, from mass balance, one must conclude that the amount of cerium deposited at the anode is virtually unchanged beyond two hours.

The percent Fe and Cu found in the aluminum pool are shown in Figure 47. It can be seen that both the Fe and Cu levels decrease with time. This behavior was not observed in any of the previous time course experiments. It must be concluded that the decrease in percent levels is a result of the continuous production of Al, which dilutes the impurities introduced at the beginning of the experiment.

When the values are adjusted for the production of Al, the total amount of Fe and Cu impurities can be plotted as a function of time. This is shown in Figure 48. Both the Fe and Cu levels are unchanged with time, indicating no measurable corrosion of the anode beyond the two hour time point. The CEROX coating produced under these conditions is extremely effective at inhibiting attack on the substrate.

Figure 49 shows the adjusted weight percent of iron deposited in the electrowon aluminum as a function of time. These data suggest, within experimental error, that the CEROX coating provides complete protection.

In contrast to the previous time course experiment, microstructural examination of the coated cermets showed no

Figure 47. Weight Percent Fe and Cu in Aluminum Pool as a Function of Time. 0.8 A/cm²; 1.5% CeO₂ Bath Concentration

Figure 48. Total Weight of Fe and Cu in Aluminum as a Function of Time. 0.8 A/cm²; 1.5% CeO₂ Bath Concentration

Figure 49. Adjusted Weight Percent of Iron Deposited in Electrowon Aluminum. 0.8 A/cm²; 1.5% CeO₂ Bath Concentration

evidence of a reaction zone. Figure 50 shows cross-sections of the samples obtained after 2, 4, 6 and 8 hours of testing, with the CeO_2 coating remaining well adherent to the cermet throughout the test. The lack of a reaction zone is consistent with the results obtained by metal analysis. Both results indicate protection of the cermet by the CERCOX coating.

In conclusion, based on chemical and microstructural evidence, it appears that the CERCOX coating, deposited under preferred conditions, is effective in preventing attack on the cermet substrate. No time dependant corrosion could be detected within the 10 hour test. Further long term tests are required to determine wear rates and to assess the long term effectiveness of the coating.

1.5% CeO₂: 0.8 A/cm²

Figure 50. Scanning Electron Micrographs of CEROX Coated Cermets as a Function of Time. 0.8 A/cm²; 1.5% CeO₂

I. Bath Compositional Effects

In earlier sections, it was demonstrated that CeO_2 can be deposited under various conditions and that the CEROX coating diminishes corrosive attack on the substrate. Under the preferred conditions, no detectable corrosion of the Cu containing nickel ferrite was evident. However, all of these tests were performed with a common electrolyte. The bath ratio was 1.35 and contained 8% Al_2O_3 and 5% CaF_2 .

Recognizing that there is no industry wide standard bath, experiments were performed to determine the effect of bath composition on the coating process and attack on the cermet. Experiments were designed to assess the influence of alumina concentration, bath ratio and LiF and MgF_2 additions. Results are summarized in the following sections.

1. Alumina Concentration Effects

In order to assess the effect of alumina concentration on the development of the CEROX coating, three experiments were performed using 4%, 5% and 6% Al_2O_3 melts at a current density of 0.8 A/cm^2 . The bath ratio was 1.35 and contained 5% CaF_2 and 1.5% CeO_2 . The cerium oxide level and current density were established based on results from previous studies (section C). As in all experiments, the aluminum and cryolite were chemically analyzed to assess anode wear and cerium partitioning. The change in the iR component of the anode potential was also used to determine the resistance associated with the development of the coating.

a. Cerium Partitioning and Coating Development

Table 11 shows the cerium levels found in the aluminum and cryolite from these tests, as well as the calculated partition

coefficients. These values (and those obtained in the time course experiments described in section I-2) are higher than that obtained with an 8% alumina bath ($5.92 + 1.87$). This indicates that a decrease in alumina significantly increases the percent cerium in the aluminum. This effect is likely due to the equilibrium established between CeO_2 , AlF_3 , Al_2O_3 and Al. To minimize the Ce levels in the aluminum pool, it appears that a cryolite melt saturated with alumina is preferred.

Table 11. Cerium Partition Coefficients as a Function of Alumina Concentration in the Bath

<u>Percent Alumina</u>	<u>Ce/Al</u>	<u>Ce/Cryolite</u>	<u>Partition Factor</u>
4.0	3.9	.38	10.3
5.0	3.4	.62	5.5
6.0	3.7	.31	11.9

b. Coating Resistance

The electrical resistance factors attributable to the development of the coating was found to be insensitive to the alumina content. Coating resistances were found to range from .52 to .56 ohm-cm². Within experimental error, these are identical, and comparable to the value obtained with the 8% alumina bath. Since the coating resistance is known to be most affected by the thickness of the CEROX layer, the electrochemical measurements indicate that thickness is insensitive to alumina concentration. This was confirmed by microstructural analysis (section I-1d).

c. Metal Purity

Figure 51 shows the effect of alumina content on the Fe and Cu levels found in the electrowon Al. From 4 to 6 percent

Figure 51. Percent Fe and Cu Levels in Aluminum as a Function of Bath Alumina Concentration. 0.8 A/cm²; 1.5% CeO₂

alumina, the Fe levels appear to increase with increasing alumina. However, the lowest levels were obtained using the 8% alumina melt (standard condition). Considering the magnitude of the iron levels found at the beginning of our tests, it is likely that this series of experiments cannot distinguish the Fe corrosion rates.

The Cu levels are also plotted against the percent alumina in the bath in Figure 51. Here, there does appear to be a detectable effect, with the Cu levels increasing as the alumina concentration decreases. This is consistent with the hypothesis that the bath must remain near saturation to passivate the Cu metal. This passivation is believed to be by formation of a copper aluminate. (5)

d. Microscopic Examination

Optical micrographs of the transverse section of the CEROX coating and the substrate produced in bath containing 4%, 5% and 6% Al_2O_3 are shown in Figure 52.

Notice the coating is porous, the pores being mostly filled with cryolite. Thickness did not depend on the alumina concentration.

The only difference microstructurally between the samples is a decreased adherence of the coating with increasing Al_2O_3 concentration. Since the Fe levels in the Al are also increasing with Al_2O_3 concentration, it is possible that the decreased coating adhesion is due to a weakening of the ferrite matrix. However, it is also possible that the coating detachment occurs during cooling after the test. In this

6% Alumina

4% Alumina

5% Alumina

Figure 52. Optical Micrographs of CEROX Coated Cermets at Varying Bath Alumina Concentration. 0.8 A/cm²; 1.5% CeO₂

case, the apparent decrease in coating adhesion may not be significant. The effect could be resolved by examining the effect of alumina in longer term tests, where anode wear rates can be established.

2. Time Course Experiment in Low Alumina Bath

In addition to the preceeding experiments, one time course experiment was performed, consisting of runs of 2, 4, 6, 8 and 10 hours. The 4% alumina bath was chosen for this experiment to provide the maximum contrast with the previous time course experiments, which were performed with an 8% alumina bath.

a. CEROX Development

As in all of the previous time course experiments, the percent cerium in both the aluminum pool and cryolite decreased with time. This is shown in Figure 53.

The fact that the percentages should change together is expected, and reflective of a constant partition coefficient. It should be noted that the cerium levels in the Al are much higher than those of previous time course experiments (section H). A partition coefficient of 11.10 ± 1.82 is calculated from these data. Again these data indicate that the partition coefficient increases with decreasing alumina content of the bath.

Figure 54 shows the amount of total cerium in both the aluminum and bath as a function of time. The fact that the cerium in the aluminum is constant is fortuitous in that the decrease in percentage is offset by the growing aluminum pool. In contrast, the depletion of cerium from the bath is

Figure 53. Percent Cerium in Bath and Aluminum as a Function of Time.
0.8 A/cm²; 1.5% CeO₂ 4.0% Alumina Bath
Concentration

Figure 54. Total Weight of Cerium in Bath and Aluminum as a Function of Time. 0.8 A/cm²; 1.5% CeO₂ 4.0% Alumina Bath Concentration

apparent. By mass balance considerations, the amount of cerium deposited at the anode can be calculated, and is also shown in the figure. It can be seen that the development of the coating is not instantaneous, but rather took several hours with this experimental setup. By ten hours, the CEROX deposition appears to be approaching steady state.

The fact that several hours are required for the coating to fully develop is also evidenced by the micrographs, shown in Figure 55. Here it can be seen that the coating thickness increases from two to six hours. Beyond 6 hours, the thickness was insensitive to time.

It is significant that the development of the CEROX coating in this experiment is slower than that seen with the 8% alumina bath. This is consistent with the proposed net anodic reaction:

A decrease in alumina concentration might be expected to decrease the rate of formation of the CEROX coating.

b. Cermet Corrosion

The percent iron and copper found in the aluminum pool as a function of time are shown in Figure 56. It is very interesting to observe that the Fe levels are decreasing, whereas the Cu levels are slightly increasing. This was not the case in our earlier work with the 8% alumina bath, in which case both Fe and Cu levels decreased (section H-2).

Because the size of the aluminum pool is changing, more insight is obtained by looking at the total amount of iron and

4% Alumina at 2 hours

4 hours

Figure 55A. Scanning Electron Micrographs of CEROX Coated Cermets as a Function of Time. 0.8 A/cm^2 ; $1.5\% \text{ CeO}_2$ 4.0% Alumina Bath Concentration

6 hours

8 hours

Figure 55B. Scanning Electron Micrographs of CEROX Coated Cermets as a Function of Time. 0.8 A/cm²; 1.5% CeO₂ 4.0% Alumina Bath Concentration

Figure 56. Weight Percent Fe and Cu in Aluminum as a Function of Time. 0.8 A/cm²; 1.5% CeO₂ 4.0% Alumina Bath Concentration

copper in the aluminum. This is shown in Figure 57. Here it appears that the total Fe is unchanged beyond 2 hours. In other words, after the fast initial corrosion, the wear of the anode, as assessed by Fe levels, cannot be detected in our tests. This was the same conclusion of our earlier test with the 8% alumina bath.

In contrast, the total Cu in the aluminum pool is increasing. This is most clearly seen in Figure 58 in which the total Fe and Cu levels are shown as a function of time for the experiments performed with 4% alumina bath and 8% alumina bath. At lower alumina levels, attack on the Cu metal phase in the cermet is enhanced. This is predicted when considering that the Cu is passivated by a copper aluminate phase. Decreasing the alumina concentration should destabilize formation of the passive layer.

When the total amount of Fe and Cu are divided by the amount of Al produced, one gets a normalized impurity level, which at steady state should be constant. Figure 59 shows the adjusted weight percent of iron deposited in the electrowon aluminum as a function of time. The plot indicates that the aluminum has an iron concentration of 0.02 weight percent, suggesting that the CEROX coating has provided nearly complete protection.

3. Effects of Bath Ratio

Four experiments were performed using bath of varying NaF/AlF₃ ratio. The control experiment was a bath (ratio 1.35) containing

Figure 57. Total Weight of Fe and Cu in Aluminum as a Function of Time. 0.8 A/cm²; 1.5% CeO₂ 4.0% Alumina Bath Concentration

Figure 58. Comparison of Time Course Experiments Performed at 0.8 A/cm² and 1.5% CeO₂ Concentration. 8.0% and 4.0% Alumina in Bath

Figure 59. Adjusted Weight Percent of Iron Deposit in Electrodeposited Aluminum. 0.8 A/cm²; 1.5% CeO₂; 4.0% Alumina Bath Concentration

5% CaF_2 , 1.5% CeO_2 and 8% Al_2O_3 . The current density was 0.8 A/cm². The three other experiments were performed with bath ratios of 1.10, 1.50 and 1.60. A summary of the metal analyses from these experiments are shown in Table 12.

Table 12. Effects of Bath Ratio and LiF and MgF_2 Bath Additions of Purity of Aluminum

<u>Bath Ratio</u>	<u>%LiF</u>	<u>%MgF_2</u>	<u>Fe (ppm)</u>	<u>Cu (ppm)</u>
1.10	0	0	5700	1800
1.35	0	0	4200	1200
1.50	0	0	6600	1700
1.60	0	0	8400	2300
1.35	3	0	5500	1600
1.35	3	3	10000	4200

As shown in the table, the impurities in the aluminum increase significantly as the bath ratio is increased to 1.50 and above. At a ratio of 1.60, the metal analyses show quite high Fe and Cu levels. Decreasing the bath ratio to 1.10 also increased the impurity levels, although not to the extent of the more basic electrolytes. The best metal analyses were actually obtained from the control experiment, ratio 1.35. Visual inspection of the cross-sectioned anodes confirm the analytical results. The most extensive cermet attack was observed in the 1.60 ratio experiment, followed by 1.50, 1.10 and 1.35. Micrographs of these samples are shown in Figure 60.

The metal and bath cerium levels are shown in Table 13. Some very interesting trends are found here. First, it can be seen that the cerium partition coefficient decreases as the bath ratio decreases. This is an expected result since the Ce levels

Bath ratio 1.10

Bath ratio 1.35

Figure 60A. Scanning Electron Micrographs of CEROX Coated Cermets Produced with Baths of Differing Ratio. 0.8 A/cm^2 $1.5\% \text{ CeO}_2$

Bath ratio 1.50

Bath ratio 1.60

Figure 60B. Scanning Electron Micrographs of CFROX Coated Cermet
Produced with Baths of Differing Ratio. 0.8 A/cm^2
 $1.5\% \text{ CeO}_2$

should be controlled by the equilibrium reaction:

An increase in the AlF_3 activity should drive the equilibrium toward the reactants, thus decreasing the partition coefficient. It is actually surprising that the coefficients do not increase even more in the neutral and basic electrolytes, 1.50 and 1.60 ratio, respectively, where the AlF_3 activity is greatly diminished.

Table 13. Effect of Bath Ratio on Cerium Partition Coefficients

<u>Bath Ratio</u>	<u>Ce(Al) %</u>	<u>Ce(Bath) ppm</u>	<u>Ce (Anode) g. Calculated</u>	<u>Partition Coeff.</u>
1.10	3.5	3300	3.53	10.61
1.35	3.3	2700	3.88	12.22
1.50	2.8	2100	4.31	13.33
1.60	3.1	2100	4.23	14.76

The coating thickness, and the calculated quantity of CeO_2 at the anode (calculated by mass balance) actually increases up to a ratio of 1.5. Beyond the 1.50 ratio, the thickness may be slightly diminished. The increase in coating thickness with increasing ratio is also an expected result since the dissolution of the CeO_2 coating involves AlF_3 .

Because AlF_3 decreases both the Ce in the aluminum and the CeO_2 coating thickness, the Ce levels in the bath are highest at low ratios and lowest in the higher ratios. Therefore, it cannot simply be concluded that decreasing the bath ratio will decrease the Ce levels in the metal, since higher bath concentrations are required to maintain the coating. In order to predict the effect of bath ratio on Ce levels in the Al, the effect of bath Ce

concentration on coating thickness at all bath ratios must be determined.

Because the CEROX coating actually improves with increasing ratio while the impurity levels also increase, it must be concluded that the effect of increasing the ratio to 1.50 or 1.60 is to greatly increase corrosion of the cermet. On the other hand, the lesser increase in impurities on reducing the ratio to 1.10 may be the result of an increase in the rate of cermet corrosion at low ratios or may be the result of diminished protection by the coating. In order to distinguish these, experiments would have to be performed in Ce free bath at ratio 1.10.

4. Effect of LiF and MgF₂ Additions

Two experiments were performed using bath containing LiF. In both experiments the bath ratio was 1.35, with 8% Al₂O₃ and 5% CaF₂. Again the current density was 0.8 A/cm² and the temperature was 950°C. All previous experiments had been conducted at 980°C. However, LiF and MgF₂ depress the liquidus temperature of cryolite melts. All experiments reported in this work were conducted at 20°C above the liquidus temperature. In the first run, 3% LiF was added; in the second run 3% LiF and 3% MgF₂ was added. A summary of the metal analyses from these experiments are also shown in Table 12.

The experiment, with both LiF and MgF₂ in the bath, produced aluminum with the highest impurity levels of any experiment conducted in the program, including experiments performed in cerium free bath. In addition, by macroscopic examination, the

corrosive attack of the substrate was more pronounced in this sample. The CeO_2 coating was found to be spalling off the substrate in areas in which the substrate attack was most pronounced. This is shown in Figure 61. Despite the spalling of the coating, the coating thickness and morphology of the coating were largely unaffected. The effect of the LiF and MgF_2 additions appears to be enhanced attack on the substrate rather than diminishing the protection from the CEROX coating. Clearly, addition of both LiF and MgF_2 are deleterious to the performance of the cermet, even when coated with CeO_2 .

It is interesting to note that the Ce partition coefficient calculated from the metal and bath analyses was far less than in the control (5.13 compared to 12.22). Thus, it appears that one benefit of these additions is to decrease the Ce in the aluminum. This could be beneficial if another substrate were employed which was not adversely affected by such additions.

The experiment in which LiF alone was added produced similar results. The Fe and Cu levels in the electrowon aluminum were higher than the control sample without LiF. Severe attack of the substrate was apparent by visual inspection. The coating thickness and morphology were essentially unchanged from the control. The partition coefficient calculated from the metal and bath analyses was also very near that of the control (11.15 compared to 12.22). Because the coating thickness and quality are essentially the same as that of the control, the deleterious effect of LiF must be due to an increased intrinsic corrosion rate

Cryolite bath with 3% LiF

Cryolite bath with 3% LiF and 3% MgF₂

Figure 61. Scanning Electron Micrographs of CEROX Coated Cermet
Produced with Bath Containing LiF and Both LiF and
MgF₂. 0.8 A/cm²; 1.5% CeO₂

of the cermet in Li containing bath. LiF does not appear to affect the CEROX coating itself.

J. Conclusions:

Based on the results of this work, it is apparent that cerium oxide coatings can be readily deposited on a variety of substrates from cryolite melts conventionally used in Hall-Heroult cells. The primary benefit of the coating is a dramatic decrease in the corrosion of the substrate. In the short term tests performed in this study, no attack on the substrate was evident under the best case conditions. The associated penalty is an additional electrical resistance added to the system, resulting in an increased cell voltage. Obviously, the benefit must be weighed against the penalty in selecting preferred operating conditions. Although loss of cerium into the aluminum pool also occurs, it is expected that a recycling process could readily be developed for commercial implementation of the technology.

Specific conclusions from our studies are:

1. Cerium oxide (CEROX) coatings can readily be deposited on both SnO_2 and copper containing nickel ferrite substrates from cryolite melts. The deposition is thermodynamically possible because of the low AlF_3 activity in cryolite melts. The cerium oxide coatings produced are doped with fluoride and tend to be porous.
2. The cerium oxide coating thickness is primarily influenced by the amount of cerium added to the bath. The thickness also appears to be dependent on current density, with thicker, more uniform coatings produced at low current density. Coating porosity also tends to

increase with increasing current density.

3. CEROX coatings effectively inhibit corrosion of SnO_2 anodes. Based on metal analyses, under best conditions a decrease in corrosion by more than an order of magnitude is possible. The protection afforded by the coating is related to the coating thickness and uniformity. For this reason, the most protective coatings are those deposited at low current density from a bath containing high levels of cerium.
4. With the copper containing nickel ferrite anodes, no measurable corrosion is observed when CEROX coatings are deposited under preferred conditions. The preferred conditions are a high bath cerium concentration and low current density.
5. In the absence of a coating, or with coatings produced at high currents and low cerium levels, corrosion of the cermet is observed. This corrosion is evidenced by a reaction zone within the substrate which grows with time. In the reaction zone, Fe is preferentially leached from the ferrite matrix and Cu is redistributed. Metal analyses also indicate a preferential leaching of Fe. Iron levels in the aluminum are generally an order of magnitude higher than the Ni levels.
6. Corrosion of the uncoated cermet increases with current density. The presence of cerium in the bath, at any concentration, diminishes the corrosion.

7. Coating resistances ranging from 0 and 0.5 ohm-cm² were measured. The most protective layers were the thickest, with the highest resistance. In commercial operation, a trade off between substrate wear and resistance should be possible.
8. Ce is generally found in the aluminum pool at a level of 1.5% to 2.5%. The partitioning of cerium between the metal and the bath is influenced by bath ratio and alumina concentration. It is expected that a cerium recycling process could readily be developed for commercial implementation of the technology.
9. Decreasing the alumina concentration in the cryolite melt increases attack of the copper metal phase in the cermet. This is believed to be due to the fact that copper is passivated by an aluminate phase.
10. Cermet corrosion is enhanced as the bath ratio is increased above 1.35. However, increasing the bath ratio increases the thickness and presumably the protective nature of the CEROX coating. Based on the present work, it is difficult to determine the effect of lower bath ratios on cermet performance. However, a lower ratio does diminish the CEROX coating thickness.
11. LiF definitely increases attack on the cermet, and would not be recommended as a bath additive. The effect of MgF₂ is unresolved.

K. Recommendations

In the present work, the protection afforded by the anodically deposited cerium oxide coatings has been demonstrated. However, because of the short duration of these tests, it is impossible to accurately establish wear rates of the cermet, coated and uncoated, under the various conditions. Obviously, knowledge of wear rates is critical to establishing anode lifetimes and the effect of bath chemistry and current density is required for selection of optimum operating conditions. It is also important to quantify the decrease in anode wear rate as a function of coating thickness. In order to quantify wear rates, it is recommended that longer term testing be performed. The test duration should be sufficient to ensure that steady state cell operation is achieved.

Since thicker coatings are likely to have a higher electrical resistance, it is expected that in commercial practice, there must be a trade off between decreased substrate wear and cell voltage. Of course, there will also be a trade off between current density and voltage and substrate wear. To address these issues, it is necessary to determine the effect of coating thickness and current density on wear rates and voltage. The following experiments are therefore recommended.

1. Wear Rates of Uncoated Cermets

Long term testing of the copper containing nickel ferrites in cerium free bath should be performed at several current densities. This would address the issue of increased productivity vs. energy consumption and anode wear rate. Wear rates should be obtained by both metal analysis and by measurement of macroscopic dimensional changes of the anode.

2. Testing of CEROX Coated Cermets

It is recommended that the wear rates of the copper containing nickel ferrites be established as a function of coating thickness and current density. Because of the data base established, it is recommended that these experiments be performed using the standard melt employed in this work. Testing at various current densities and coating thicknesses would address the trade off between voltage and anode wear at various production levels. Testing at high current density and thin CEROX coating thickness would also permit the further investigation of the reaction zone development within the cermet.

3. Testing of Coated Cermets in Low Ratio Bath

The results of the present work clearly indicate that corrosion of the cermets increase as the bath ratio increases. However, the effect of lower bath ratios on the wear rate of coated cermets remains unresolved. It is expected that the long term testing of cermets in cerium-free bath would identify an optimum bath ratio for the cermet. Further decreases in the wear rate should be achieved through use of a CEROX coating. Further testing should be performed to quantify the anode wear rate as a function of coating thickness and current density. This would likely lead to the preferred operating conditions of the CEROX coated cermet anode.

4. Bath Compositional Effects

Further long term testing should be performed using cryolite melts which are not saturated with alumina. A potential benefit of the CEROX coating would be to decrease anode wear in alumina depleted bath. This would represent major technical accomplishment and a step toward commercialization of the inert anode technology. Presently, cermet operation requires a saturated bath, which is difficult or impossible to maintain in a commercial practice. In addition, further testing to determine the effect of bath additives such as CaF_2 and MgF_2 are warranted.

5. Cathode Effects

Earlier work (5) has suggested that the wear rate of the anode may be influenced by the surface area of the cathode. The rationale was that anode dissolution is controlled by the difference between the bath concentration of the cermet constituents and the solubility limit. Since the cathode surface area influences the rate of removal of dissolved Fe, Ni and Cu from the bath, steady state kinetics suggests that it should influence the bath concentration and, therefore, the anode wear rate.

In order to apply the results of long term laboratory testing to potential commercial practice, the effect of cathode surface area must be understood. Therefore, it is recommended that experiments be performed with varying cathode surface areas. This should result in a standard cathode area/anode area ratio which would then be established for all future work.

References

1. Grjotheim, K.; Krohn, C.; Malinovsky, M.; Matiasovsky, K. and Thonstad, J.; "Aluminum Electrolysis Fundamentals of the Hall-Heroult Process," 2nd Edition, Aluminum-Verlag, Dusseldorf (1982).
2. Billehaug, K. and Oye, H. A.; "Inert Anodes for Aluminum Electrolysis in Hall-Heroult Cells," Aluminum 57 (2), 146-150 (1980).
3. Billehaug, K. and Oye, H. A.; "Inert Anodes for Aluminum Electrolysis in Hall-Heroult Cells," Aluminum 57 (3), 228-231 (1980).
4. Horinouchi, K.; Tachikawa, N. and Yamada, K., "DSA in Aluminum Reduction Cells," Proceedings of the First International Symposium on Molten Salt Chemistry and Technology, Kyoto, Japan, (April 22-22, 1983).
5. Weyand, J. D.; Ray, S. P.; Baker, F. W.; DeYoung, D. H. and Tarcy, G. P.; "Inert Anodes for Aluminum Smelting," Final Report Feb. 1986; DOE/CS/40158-20.
6. Duruz, J. J. and NeNora, V.; "The Dynamic Equilibrium of a Self-Forming Anode," presented at the Meeting of the Electrochemical Society.
7. A Survey of Potential Processes for the Manufacture of Aluminum, Arthur D. Little, INC., ANL-OEPM-79-4.
8. Baker, F. W. and Rolf, R. L., "Hall Cell Operation with Inert Anodes" in Light Metals 1986, R. E. Miller (ed.) The Metallurgical Soc. Warrendale, PA (1986).
9. Belyaev, A. I. and Studentsov, Y. E., Legkie Metally 5 (3), 15 (1936).
10. Belyaev, A. I. and Studentsov, Y. E., Legkie Metally 6 (3), 17 (1937).
11. Kronenberg, M. L.; J. Electrochem Soc. 116, 1160 (1969).
12. Gadeau, R.; Bull. Soc. Fr. Electrician 7, 540 (1974).
13. Stender, V. V. and Trofimenko, V. V.; Khim. Tekhnol 12, 41, (1969).
14. Belyaev, A. I., Legkie Metally 7 (1), 7 (1938).
15. Alder, H. P., US Patent 4,057,480 Nov. 8, 1977.
16. Thonstad, J., Can. J. Chem. 43, 3429 (1965).

17. Yoshida, K. and Dewing, E. W., Met. Trans. 3, 1817 (1972).
18. Alder, H. P., US Patent 3,960,678 June 1, 1976.
19. Alder, H. P., US Patent 3,974,046 Aug. 10, 1976.
20. Ray, S. P., US Patent No. 4,374,050 Feb. 15, 1983.
21. Tarcy, G. P., "Corrosion and Passivation of Cermet Anodes in Cryolite-Type Electrolytes" in Light Metals 1986, R. E. Miller (ed.) The Metallurgical Soc. Warrendale, PA (1986).
22. Ray, S. P., US Patent No. 4,374,761.
23. Ray, S. P., "Inert Anodes for Hall Cells" in Light Metals, 1986, R. E. Miller (ed.) The Metallurgical Soc. Warrendale, PA (1986).
24. Duruz, J. J. and Derivaz, J. P., US Patent 4,397,729.
25. DeNora, V.; Spaziante, P. M. and Nidola, A., US Patent 4,098,669.
26. Duruz, J. J.; Derivaz, J. P.; Debely, P. and Adorian, J., EP-A-0114085.
27. Piontelli, R.; Mazza B, ; and Pederferri, P.: Electrochem. Acta. 10 1117 (1965).
28. Burgman, J. W.; Leistra, J. A. and Sides, P. J.: J. Electrochem. Soc. 133 (3), 496 (1986).
29. McLeod, A. D.; Haggerty, J. S.; and Sadoway, D. R.: "Inert Anode Materials for Hall Cells" in Light Metals 1986, R. E. Miller (ed.) The Metallurgical Society Inc. Warrendale Pa. (1986).