18J

Inert Electrodes Program

The Effects of Microstructure on the Corrosion of Glycine/Nitrate Processed Cermet Inert Anodes: A Preliminary Study

July 1991

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

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

DISCLAIMER

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

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

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831;
prices available from (615) 576-8401. FTS 626-8401.

Available to the public from the National Technical Information Service,
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

On the cover:

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

Inert Electrodes Program

THE EFFECTS OF MICROSTRUCTURE ON THE CORROSION OF
GLYCINE/NITRATE PROCESSED CERMET INERT ANODES:
A PRELIMINARY STUDY

C. F. Windisch, Jr.
L. A. Chick
G. D. Maupin
N. D. Stice

July 1991

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

Pacific Northwest Laboratory
Richland, Washington 99352

PREFACE

The Inert Electrodes Program at the Pacific Northwest Laboratory (PNL)^(a) is supported by the Office of Industrial Processes of the U. S. Department of Energy and is aimed at improving the energy efficiency of Hall-Heroult cells through the development of inert anodes. The inert anodes currently under study are composed of a cermet material of the general composition $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$. The program has three primary objectives: a) to evaluate the anode material in a scaled-up, pilot cell facility, b) to investigate the mechanisms of the electrochemical reactions at the anodes surface, and c) to develop sensors for monitoring various anode and/or electrolyte conditions. This report covers the results of a portion of the studies on anode reaction mechanisms.

The anode mechanism studies were focused in four areas in FY 1990 and FY 1991: a) the determination of whether a film formed on cermet inert anodes and (if it existed) the characterization of this film, b) the determination of the sources of the anode impedance, c) the evaluation of the effects of silica and a precorroded state on anode corrosion, and d) a preliminary study on the effect of microstructure on the corrosion properties of the anodes. This report discusses the results of the microstructure studies.

(a) PNL is operated for the U. S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

SUMMARY

The objective of this work was to fabricate and test cermet inert anodes with *significantly different* microstructures in order to determine whether the microstructure influences the corrosion properties of the anode. If corrosion properties are influenced by the microstructure, this study would suggest ways the microstructure can be improved to reduce the corrosion rate.

The glycine/nitrate process (GNP) was the method of choice for making the cermet inert anodes with microstructures significantly different than that of the cermet anodes previously studied by PNL. Use of this approach was promising since it had already produced very fine-grain microstructures for other ceramic systems and had the potential for being able to fine-tune various compositional and microstructural aspects of the cermet. These preliminary studies indicated that the method can be used to fabricate anodes with very small grains, on the order of 1 μm . However, some of the anodes made with this approach were also very different *compositionally* from the standard cermet anodes. Additional work is still required to tune the fabrication parameters so as to achieve, reproducibly, a chemical composition of the cermet phases that is more similar to that of the standard cermet anodes (with only the scale of the microstructure different). Only in this way can the effects of microstructure scaling be separated unambiguously from the effects of chemical composition of the various cermet phases.

Electrochemical testing of the GNP anodes resulted in severe degradation of the anodes. The mode of attack appeared to be along grain boundaries and was characterized by changes in the physical and electrical properties of the anode as well as in the composition and distribution of the cermet phases. Raising the current density on the anode appeared to increase the amount of corrosion of the metal phase as well as the dissolution/reaction of the oxide phases.

These preliminary results suggest that successful cermet anodes will have larger grain sizes or a composition that somehow restricts access of the electrolyte along grain boundaries. Future work is recommended to determine better compositional and microstructural effects on the corrosion of the GNP

anodes and to investigate, using more fundamental approaches, the mode of attack along grain boundaries. Since the standard anodes showed very little corrosion in these tests, evaluation of coarse-grain anodes would appear to be more suited to larger pilot-scale or industrial-scale cells that can be operated uniformly for much longer periods of time than is possible with bench-scale cells.

ACKNOWLEDGMENTS

The authors wish to acknowledge the technical assistance of PNL staff including N. C. Davis for preparing the standard cermet anodes, N. T. Saenz for the microscopy work, D. E. McCready for x-ray diffraction (XRD), and J. E. Coleman for scanning electron microscopy (SEM); and the editorial assistance by D. K. Hilliard. The programmatic support provided by L. G. Morgan and initial suggestions on using the GNP approach by G. L. McVay are also recognized. Finally, the authors are grateful for the financial support for this work by the Office of Industrial Processes (OIP), U.S. Department of Energy (DOE), and the program direction provided by the DOE-OIP manager, M. J. McMonigle.

CONTENTS

PREFACE	iii
SUMMARY	v
ACKNOWLEDGMENTS	vii
1.0 INTRODUCTION	1.1
2.0 FABRICATION OF THE GNP ANODES	2.1
2.1 GLYCINE-NITRATE COMBUSTION	2.1
2.2 REDUCTION	2.2
2.3 PRESSING	2.5
2.4 SINTERING	2.5
3.0 ELECTROCHEMICAL TESTING OF GNP ANODES WITH FINE GRAINS	3.1
3.1 APPROACH	3.1
3.2 EXPERIMENTAL PROCEDURE	3.2
3.3 RESULTS AND DISCUSSION	3.5
3.3.1 Behavior During Electrolysis	3.5
3.3.2 Microscopic Analysis	3.17
3.3.3 Bloating	3.17
3.3.4 Compositional Changes	3.17
3.3.5 Porosity	3.23
3.3.6 Effects of Microstructure	3.34
4.0 CONCLUSIONS	4.1
5.0 REFERENCES	5.1

FIGURES

2.1	Stability Diagram for Oxides in the Inert Anode Composite System	2.2
2.2	X-Ray Diffraction Patterns for the GNP Oxide Ash (Top) and the Powders After Reducing Heat Treatments at 200°C (Middle) and 400°C (Bottom)	2.3
2.3	X-Ray Diffraction Peak for the 200 Planes in the Metallic Phase	2.4
2.4	Microstructures of Sintered Anode Samples	2.7
3.1	Laboratory Apparatus for Short-Term Parallel Testing	3.3
3.2	Variation of ΔV_2 with Time During Electrolysis in STP Tests at 1 A/cm ² and 0.5 A/cm ²	3.6
3.3	Relationship Between the <i>Initial</i> ΔV and Current Density in the STP Tests	3.8
3.4	Comparison at 6.5X Magnification of a) Standard Anode STD-11 ₂ and b) GNP Anode LC-1 after Electrolysis at 1 A/cm ² for 6 h	3.9
3.5	Comparison at 6.5X Magnification of a) Standard Anode STD-12 ₂ and b) GNP Anode LC-9 after Electrolysis at 1 A/cm ² for 6 h	3.10
3.6	Comparison at 6.5X Magnification of a) Standard Anode STD-13 ₂ and b) GNP Anode LC-12 after Electrolysis at 1 A/cm ² for 6 h	3.11
3.7	Comparison at 6.5X Magnification of a) Standard Anode STD-14 and b) GNP Anode LC-11 after Electrolysis at 0.5 A/cm ² for 6 h	3.12
3.8	Comparison at 250X Magnification of a) Standard Anode STD-11 ₂ and b) GNP Anode LC-1 after Electrolysis at 1 A/cm ² for 6 h	3.13
3.9	Comparison at 250X Magnification of a) Standard Anode STD-12 ₂ and b) GNP Anode LC-9 after Electrolysis at 1 A/cm ² for 6 h	3.14
3.10	Comparison at 250X Magnification of a) Standard Anode STD-13 ₂ and b) GNP Anode LC-12 after Electrolysis at 1 A/cm ² for 6 h	3.15

3.11	Comparison at 250X Magnification of a) Standard Anode STD-14 and b) GNP Anode LC-11 after Electrolysis at 0.5 A/cm ² for 6 h	3.16
3.12	Variation in Thickness of Metal-Depleted Region for Electrolyzed Anodes as a Function of Current Density	3.18
3.13	Schematic of Layers of Various Compositions in GNP Anodes after Electrolysis	3.20
3.14	Porosity of Bottom Region of Standard Anode STD-11 after Electrolysis at 1 A/cm ² for 6 h	3.24
3.15	Porosity of Bottom Region of Standard Anode STD-12 after Electrolysis at 1 A/cm ² for 6 h	3.25
3.16	Porosity of Bottom Region of Standard Anode STD-13 after Electrolysis at 1 A/cm ² for 6 h	3.26
3.17	Porosity of Bottom Region of Standard Anode STD-14 after Electrolysis at 0.5 A/cm ² for 6 h	3.27
3.18	Porosity of Bottom Region of GNP Anode LC-1 after Electrolysis at 1 A/cm ² for 6 h	3.28
3.19	Porosity of Bottom Region of GNP Anode LC-9 after Electrolysis at 1 A/cm ² for 6 h	3.29
3.20	Porosity of Bottom Region of GNP Anode LC-12 after Electrolysis at 1 A/cm ² for 6 h	3.30
3.21	Porosity of Bottom Region of GNP Anode LC-11 after Electrolysis at 0.5 A/cm ² for 6 h	3.31
3.22	Relationship Between Current Density and Porosity in Corner Sections of Electrolyzed GNP Anodes	3.32
3.23	Relationship Between Current Density and Porosity in Bottom Sections of Electrolyzed GNP Anodes	3.33
3.24	Relationship Between Current Density and Porosity in Center Sections of Electrolyzed GNP Anodes	3.34
3.25	Bar Graph Summarizing Porosities Measured at Various Locations for Electrolyzed GNP Anodes	3.35
3.26	SEM Micrograph and EDS Elemental Aluminum Distribution Maps for GNP Anode LC-9 after Electrolysis	3.36

3.27	Plot of Grain Size Versus Porosity in the Center of Anodes Electrolyzed at (a) 1 A/cm^2 and (b) 0.5 A/cm^2		3.38
3.28	Plot of Grain Size Versus Porosity in the Corner of Anodes Electrolyzed at (a) 1 A/cm^2 and (b) 0.5 A/cm^2		3.38

TABLES

2.1	Anode Microstructural Parameters	2.8
3.1	Identification and Pre-Electrolysis Properties of Anodes Used in Electrolysis Cells	3.4
3.2	Area Percentages of Phases Using Image Analysis	3.22

1.0 INTRODUCTION

During FY 1990 and FY 1991, electrochemical testing on cermet inert anodes at PNL gave evidence that the microstructure and morphology of these anodes were important in determining certain operational characteristics related to anode longevity and energy efficiency. It was determined (Windisch and Stice 1991a) that the dissolution and corrosion of the three principal phases of the cermet material were not uniform. The metallic phase was shown to corrode out of the surface region of the anode during very early times after the start of electrolysis. The two oxide phases were also shown to exhibit different tendencies to dissolve or react at the anode surface. Because of the differential properties of the three phases, it was thought that a more "hardy" electrode could be achieved by changing the microstructure or distribution of the three phases. For example, it appeared from the earlier studies that, at least in the early stages of polarization, the NiO particles "fell out" of the ceramic matrix as the spinel phase dissolved around it. By making the microstructure smaller, a finer-perhaps more interconnected - "mesh" of the less soluble NiO network might be achieved. As a consequence, the fine "net" of NiO might serve as an effective barrier to the ingress of electrolyte into more reactive (more metal-rich) interior regions of the anode.

In addition to studies on the reactivities of the various phases in the cermet anodes, other studies were performed (Windisch and Stice 1991b) to characterize the sources of the anode impedance. This work showed that one of the principal sources of the impedance was gas bubbles generated at the anode during electrolysis of the molten salt. Moreover, the impedance due to gas bubbles was found to depend on the morphology (e.g. roughness) of the anodes. In a parallel set of studies (Windisch and Stice 1991a), it was shown that the morphology developed on an operating anode could be strongly influenced by the anode's original microstructure. All of this points to the importance of understanding the effects of microstructure on operating characteristics. A certain microstructure may favor a surface structure that yields optimal operational efficiency, i.e., the lowest impedance or associated voltage drop.

Anode microstructure appeared to be an important factor in determining the properties of cermet inert anodes as discussed above. However, these previous studies were *not focused* on the effects of microstructure. Rather, its effects were inferred from patterns of behavior on one type of microstructure only. Consequently, it was proposed in this work that anodes having *two very different* microstructures be prepared, tested, and compared in carefully designed cells. A comparison of the performance of anodes with the two very different microstructures (with all other conditions constant) would determine a) whether the microstructure of the anode played as important a role as anticipated from the previous work, and b) what changes in direction, if any, should be taken in fabrication (i.e., to finer or coarser microstructures) in order to optimize anode performance. In this study, anode performance was interpreted largely in terms of the extent of degradation of the anodes under a specific set of operating conditions.

The types of microstructures evaluated in this work were determined by the fabrication methods available at the time. "Course" microstructure anodes (grain size of 10-20 μm) were prepared using the standard fabrication methods already developed at PNL (Strachan et al. 1988). Anodes with this microstructure were called "standard anodes." Anodes with "fine" microstructure (grain size about 1 μm) were prepared using the GNP method that had been developed at PNL for other ceramic systems and showed promise for the inert anode cermet system as well. These anodes were called the "GNP anodes."

The electrolysis tests used to compare the anodes were designed to eliminate the effects of variations in other cell parameters. In these tests, a standard anode was run in parallel with a GNP anode, in the same cell, under the same conditions, and for the same length of time. After the tests, the anodes were examined using a combination of microscopic and elemental analytical techniques with the objective of relating the extent of degradation of the anode (under a specific set of cell operating conditions) to its microstructure.

It should be emphasized that this work is preliminary in scope. In all, only four anodes made by the GNP method were tested under electrolysis conditions. Of these four anodes, one had a different chemical composition. Of

the remaining three, one was tested at a different current density. Because of the paucity of anodes and conditions tested, it was difficult to develop precise relationships between the microstructures of the anodes and performance. Nevertheless, this work was successful in showing the basic results of going to a fine microstructure, as prepared using the GNP method. Where sufficient evidence was present (as in the case of anode porosity), some indications of relationships involving microstructure were *inferred*. But again, these inferences should be viewed with some caution. Clearly, further testing using GNP anodes is required to quantify, with reasonable precision, any correlation between microstructural parameters and the behavior of the cermet inert anodes.

The following report is divided into two major parts. In Part I, the GNP method for fabricating the fine-grain anodes is described in detail and the microstructures and properties of the GNP anodes are discussed. In Part II, the specific approach to electrolysis testing of the GNP anodes is described and the results of this testing are reported.

2.0 FABRICATION OF THE GNP ANODES

This section discusses the fabrication procedures involved in the GNP process and some of the microstructural and physical properties of the GNP anodes made in these preliminary studies.

2.1 GLYCINE-NITRATE COMBUSTION

The powder synthesis technique used, GNP, is described elsewhere (Chick et al. 1990). To summarize the GNP, metal nitrates of appropriate proportions for the desired product are dissolved in water along with the amino acid, glycine. Excess water is evaporated by boiling. During evaporation, the glycine serves to prevent premature precipitation of the metal nitrates, allowing them to remain intimately mixed on a molecular scale. When most of the free water has been removed, the solution becomes increasingly viscous and bubbles begin to form. When the boiling temperature nears 200°C, the precursor solution (consisting of both fuel [glycine] and oxidant [nitrates]) ignites and burns, leaving an ash composed of fine particles of the desired product.

Powders were prepared by the GNP under three fuel/oxidant (redox) conditions: fuel-rich, stoichiometric, and fuel-lean. The stoichiometric condition is that calculated to yield N_2 , CO_2 , and H_2O as the sole gaseous products of combustion, and has been found to give the highest flame temperature (Chick et al. 1990). Fuel-rich used twice and fuel-lean used half of the amount of glycine required for the stoichiometric condition. The fuel-rich and the stoichiometric conditions both produced powders containing a Ni-Fe metal phase, NiO, CuO, and $NiFe_2O_4$, as determined by X-ray diffraction (XRD). The fuel-lean combustion produced CuO, NiO and $NiFe_2O_4$. XRD line-broadening measurements and transmission electron microscopy determined that the fully oxidized powders (fuel-lean) had significantly smaller particle size than those containing the metal phase. Excessive particle growth under the fuel-rich and the stoichiometric combustion conditions may have been due to melting or sintering of the Ni-Fe metal phase. Because the objective was to produce a fine-grained composite structure, further work utilized the fully oxidized

powders produced by fuel-lean combustion. This necessitated a heat treatment to reduce the CuO, but this could be conducted at a low enough temperature to prevent melting and excessive particle growth, thus maintaining the desired fine particle size.

2.2 REDUCTION

After combustion to produce the fully oxidized ash, the powder was heated in an atmosphere containing 4% H_2 in Ar in order to reduce the CuO to Cu metal. Figure 2.1 is a stability diagram for the system. Although the exact position of the boundary for spinel ($NiFe_2O_4$) is unknown, it is certainly below that for Ni/NiO. Therefore, the space between the Ni/NiO and the Cu/Cu₂O boundaries indicates the range of temperature/redox conditions that

FIGURE 2.1. Stability Diagram for Oxides in the Inert Anode Composite System. (Shows temperature - oxygen partial pressure regions wherein the pure phases are stable. Exact position of the spinel stability boundary is unknown.)

should yield the desired phases. Figure 2.2 shows XRD patterns for oxide ash (top) and for two different reducing heat treatments. Eight hours at 200°C in Ar + 4%H₂ reduced the CuO to Cu metal, but left the NiO and NiFe₂O₄ intact, whereas a similar treatment at 400°C reduced all of the oxides to a single cubic metal phase.

FIGURE 2.2. X-Ray Diffraction Patterns for the GNP Oxide Ash (Top) and the Powders After Reducing Heat Treatments at 200°C (Middle) and 400°C (Bottom). (Reduction at 200°C converts the CuO to pure Cu metal. Reduction at 400°C converts all of the oxides to metal.)

Intermediate temperature reductions result in the partial incorporation of Ni into the Cu metal phase. This is illustrated in Figure 2.3, which is detail of the XRD peak for the {200} planes of the metal phase. Both Cu and Ni metals have the face centered cubic (FCC) structure and are nearly the same size so that they are continuously soluble in one another. However, since the Cu atom is slightly larger than Ni, the Cu unit cell is 2.6% larger than that for Ni. As a result, the 200 line for pure Cu will occur at 50.43 degrees, whereas that for pure Ni is at 51.84 degrees (2θ). Therefore the measured position of this peak can be used to indicate the amount of Ni that has been

FIGURE 2.3. X-Ray Diffraction Peak for the 200 Planes in the Metallic Phase. [Increasing the temperature of the reducing heat treatment (200° to 235° to 265°C) results in shifting of the peak position, indicating that NiO is being reduced and Ni is being incorporated into the Cu metal phase.]

reduced and dissolved into the metal phase. Figure 2.3 indicates that a 200°C reduction yields essentially pure Cu metal, whereas a 265°C reduction yields a metal phase containing approximately 50% Ni. The fact that the left-hand sides of these peaks are in nearly identical positions indicates that the powders containing Ni are probably not homogeneous, but contain some particles with pure Cu and some with substantial concentrations of Ni in the metal phase. These results clearly indicated that 200°C is the proper temperature for reduction of the GNP ash to give pure Cu metal, NiO, and NiFe_2O_4 . Production of powder having the nominal composition of the standard anodes (10-15% Ni in the metal phase) requires an intermediate temperature, near 235°C.

2.3 PRESSING

After completion of the desired reducing heat treatment, the powder was allowed to cool to room temperature and then transferred to a glove box for further handling under nitrogen. It was found that transfers into the glove box had to be performed rapidly, even when the powder had cooled to room temperature, in order to prevent "burn-back," the spontaneous re-oxidation of the powder (Cu to CuO or Cu_2O). After transfer, the powder was loaded into a rubber bag and transferred to an isostatic press wherein it was preslugged to 2000 psi. Back in the glove box, the preslugged lumps were broken down to pass through a 45 mesh sieve. The preslugged powder was then loaded into a 1-in.-dia. steel die for uniaxial pressing at 5000 psi. Finally, the resulting pellets were isostatically pressed at 20000 psi.

2.4 SINTERING

If the powder within the pressed pellet has had the correct reducing heat treatment and has been protected from contact with the atmosphere so that burn-back did not occur, then the desired final phases and phase proportions should be present within the unsintered (green) pellet. The requirement for sintering is then to maintain those phases and densify the sample. Referring to the stability diagram (Figure 2.1) the P_{O_2} should ideally be adjusted to follow a desired path as the sample is heated and cooled during sintering. In the present investigation, however, the only gases available for use were

Ar + 4% H_2 and dry N_2 . An oxygen monitor was available, but this instrument was insensitive below 0.1 ppm O_2 . Therefore, the sintering atmosphere and sintering schedule for these studies were at best compromises arrived at by trial and error. The sintering conditions used resulted in further reduction of the samples for the two types of samples actually tested in electrochemical cells. That is, in both cases the powders were heat treated at 200°C and contained no Ni in the metal phase prior to sintering. However, in both cases some Ni was incorporated into the metal phase during sintering. In the first case, about 5% Ni was incorporated; in the second case, about 12% was incorporated.

Figure 2.4(a) shows the microstructure of a typical anode made by the standard powder metallurgy method. Figures 2.4(b) and 2.4(c) illustrate the microstructures of samples produced by the GNP method; these microstructures are believed to be similar to the two types that were tested in electrolysis cells.^(a) Sample Sint#3, shown in Figure 2.4(b), was intended to replicate the nominal composition of the standard anodes and was produced by the following sintering schedule:

1. Heat at 200°C/h to 340°C in Ar with 4% H_2 .
2. Switch to dry nitrogen (Zr-gettered) and continue heating at 200°C/h.
3. Hold at 1130°C for 1 h in dry nitrogen.
4. Cool to room temperature in dry nitrogen at 200°C/h.

As discussed in Section 3.3, a sample (LC-1) similar to that shown in Figure 2.4(b) was tested in an electrolysis cell and was found to have high resistivity and to rapidly corrode and swell. It was thought that the extra voltage required to run this electrode might have contributed to its rapid corrosion rate. Therefore, the next electrodes produced were designed to have higher total metal content, in order to decrease the resistivity. This led to production of samples with microstructures similar to Sint#10, shown in Figure 2.4(c), which was sintered by the following steps, *all performed in dry nitrogen*:

(a) The correspondence between samples sacrificed for microscopy prior to testing and samples actually tested in electrolysis cells is detailed in Section 3.2.

FIGURE 2.4. Microstructures of Sintered Anode Samples: a) Standard Anode Prepared by Powder Metallurgy, b) Anode with Nominal Composition Similar to the Standard Anode but Prepared by the GNP Method (Sint#3), c) Anode with High Metal Content Prepared by the GNP Method (Sint#10). (Microstructural data are shown in Table 2.1.)

TABLE 2.1. Anode Microstructural Parameters

Parameter	Standard [4(a)]	Sint#3 [4(b)]	Sint#10 [4(c)]
Vol% NiFe_2O_4	66	64	58
Vol% NiO	19	19	11
Vol% Metal	13	13	28
%Ni in Metal	12.5	11	7
Vol% Porosity	2	4	3
Grain Size (μm) ^(a)	11 +/- 9	0.9 +/- 0.5	1.7 +/- 1.0

(a) Grain size is here defined as the diameter of grains of the metal phase when envisioned as equivalent spheres.

1. Heat at 200°C/h to 1080°C.
2. Hold for 1 h at 1080°C.
3. Cool to room temperature at 200°C/h.

Table 2.1 shows a data summary of the microstructures that are shown in Figure 2.4. The data were obtained using image analysis and immersion densities.

In each case, the scale of the GNP-produced microstructures [Figures 2.4(b) and 2.4(c)] is significantly smaller than that of the standard [Figure 2.4(a)]. On a linear basis, the GNP microstructural scale is about an order of magnitude smaller, as exemplified by the data for equivalent spherical diameters in the last line of Table 2.1. On a volume basis, the GNP particles within the composite are about three orders of magnitude smaller. Perhaps more importantly, the *surface area* of the grains, and therefore the total grain boundary content of the GNP-produced material is about an order of magnitude *greater* (per unit volume) than for the standard anode.

The Sint#4 material is remarkably similar to the nominal composition of the standard anode except for its smaller scale. The Sint#10 material contains significantly higher total metal phase volume, as intended. Because the GNP-produced powders are so much finer and more reactive than the traditional powders, the GNP electrodes can be sintered at lower temperatures (1080° to

1130°C), below the melting point of the metal phase. This prevents the "bleeding out" of the metal phase, even when it is present at high volume fraction.

1. The melting point of the metal phase. This process is
directed out of the metal phase, even when it is present at high volume

in the

3.0 ELECTROCHEMICAL TESTING OF GNP ANODES WITH FINE GRAINS

This section discusses the electrochemical testing of cermet inert anodes fabricated using the GNP approach. The rationale for the testing program is first explained; this is followed by a description of the experimental setup used; finally, the experimental results are presented and discussed in detail.

3.1 APPROACH

Numerous laboratory or bench-scale studies on cermet inert anodes have been performed at PNL over the past six years. Typically, in these tests, a single anode was polarized and the cell operated for some period of time while trying to maintain cell conditions as uniform as possible for the duration of the test. The uniformity in operation was needed so that the results of the test, in particular the performance of the anode as measured by its post-test appearance, could be correlated with the cell operating conditions. For many of the laboratory tests, especially those using larger cells over an extended period of time, ensuring uniformity in operation was not trivial. Bath additions, adjustments to anode height, and intrusive measurements are all required at various times to monitor and maintain cell conditions. Each of these operations, in turn, has the potential for disturbing the anode in some way and, hence, influencing the test results.

One effective way to remove uncertainties associated with cell operation is to run two anodes in parallel *in the same cell*. This approach is especially useful when two different anodes are to be evaluated or compared at the same current density in an electrolyte with exactly the same composition. An electrode with some novel composition or microstructure would be run in parallel with a *standard* anode. Any differences in performance between the two could then be attributed to the compositional or microstructural differences between the anodes.

A parallel testing scheme was used in this work to compare the GNP anodes with the standard anodes that have been under study at PNL for the past six years. The standard anodes were fabricated using methods reported

previously (Strachan et al. 1988) and have a grain size on the order of 10 to 20 μm . Because the studies reported here were also relatively short in duration (about 6 h), they are referred to as short-term parallel (STP) tests.

3.2 EXPERIMENTAL PROCEDURE

The STP apparatus is shown in Figure 3.1. In this arrangement, two power supplies were used to drive each of the two anodes separately. The carbon cell was used as the common cathode lead for both circuits and grounded. For every test in this study, both anodes were positioned in the cell at a similar position with respect to each other and to the cell bottom and sidewalls: each anode was 0.75 in. from the cell bottom; and there was 1.0 in. between the center of each anode and the nearest sidewall, and 1.0 in. between the centers of the two anodes.

The anodes were in the form of small cylinders and were sheathed with boron nitride (BN) to allow exposure of only 1 cm^2 of surface area to the electrolyte. The standard anodes were fabricated according to methods discussed in previous PNL reports (Strachan et al. 1988); the GNP anodes were prepared as discussed in Section 2.0 of this report. The lead wire arrangement was different for the two types of anodes because the GNP anodes were not as long as the standard anodes. In the case of the standard anodes, a 0.125-in. Ni rod was brazed into a hole in the cermet using methods reported previously (Strachan et al. 1988). For the GNP anodes, a groove was machined around the circumference of the anode about 0.25 in. from the end furthest away from the electrode/electrolyte interface. 20-mil platinum wire was wrapped around the anode, within this groove, and then channeled up through the BN sheathing tube. (a)

The composition of the molten cryolitic bath was the same for all anodes tested. It was prepared by mixing national Greenland cryolite (Na_3AlF_6) with appropriate amounts of reagent grade materials to give a bath ratio equal to

-
- (a) A significant voltage drop was measured between the Pt lead wire and the bottom surface of the GNP anode in all cases, but this was attributed to the properties of the GNP anode itself (see Section 3.3.1) and not the electrical connection.

FIGURE 3.1. Laboratory Apparatus for Short-Term Parallel (STP) Testing.

1.15, 5.5% (by weight) CaF_2 , 1.0% MgF_2 , and 8.0% Al_2O_3 (saturation). A temperature controller/furnace/ thermocouple arrangement was used to melt the raw materials to form the bath and control its temperature throughout each experiment at 983°C. Bath ratio has been shown to remain essentially constant during these types of experiments (Windisch and Stice 1991a).

Using the two power supplies, the current was controlled to give the desired current density on the anodes. In a given test, the current density on the two anodes was always the same. Experiments were run at 1.0 A/cm^2 and 0.5 A/cm^2 . In these experiments, no significant interference was ever observed between the two power supplies. The duration of all of the tests in this study was about 6 h at the controlling current density. During each test, the voltage and the current for each anode were recorded using a multipen strip-chart recorder.

Only four GNP anodes were tested in this work. The identification numbers, characteristics and test conditions of these anodes are given in Table 3.1. Other pre-electrolysis properties of these anodes can be *inferred* from the properties of anodes prepared under similar conditions but sacrificed for structural/compositional analysis. In particular, anode LC-1 was

TABLE 3.1. Identification and Pre-Electrolysis Properties of Anodes Used in Electrolysis Cells

Anode ^(a)	Similar Sacrificed ^(b) Anode	Standard Anode in Parallel	Bulk Density, g/cm^3	Current Density, A/cm^2
LC-1	Sint#3	STD-11	5.921	1.0
LC-9	Sint#10	STD-12	6.440	1.0
LC-11	Sint#10	STD-14	6.434	1.0
LC-12	Sint#10	STD-13	6.458	0.5

(a) The anode designations LC-1, LC-9, LC-11 and LC-12 were used for the electrochemical tests. These anodes are the same as Sint#4, Sint#9, Sint#11 and Sint#12, respectively. The latter designations were assigned during fabrication.

(b) Refer to Table 2.1 for properties of sacrificed anodes.

considered similar to Sint#3 while anodes LC-9, LC-11, and LC-12 were considered equivalent to Sint#10. The properties of Sint#3 and Sint#10 are given in Table 2.1.

After the test was over, the anodes were removed from the bath while still under polarization conditions and then the voltages were shut off. Subsequently, both the standard and GNP anodes were submitted for post-mortem analyses using optical microscopy, image analysis, scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopic (EDS) analysis.

3.3 RESULTS AND DISCUSSION

3.3.1 Behavior During Electrolysis

Cell voltages and currents (across or through both the standard and GNP anodes) were monitored during the 6-h tests. The currents were under instrumental control and, therefore, uneventful. The voltages across the standard anodes were also steady and relatively quiet. In contrast, the voltages across the GNP anodes showed some noise and, more importantly, varied systematically during the test in a way that depended on the anode and the current density. Figure 3.2 shows the variation of the difference between the cell voltages, ΔV , between the GNP and standard anodes for each of the four electrolysis tests.

As shown in Figure 3.2, ΔV for all of the GNP anodes is relatively high throughout the tests, indicating a high resistivity for the GNP anode materials. This surprising result became apparent when the first GNP anode, LC-1, was tested. Subsequently, the room temperature resistivity of Sint#3 (the analog to LC-1 that was sacrificed for characterization) was measured and found to be about 0.3 ohm cm or about an order of magnitude higher than the standard anode material. If the LC-1 material had a resistivity of 0.3 ohm cm, it can be shown that LC-1 should give a ΔV equal to about 0.5 V, which is very close to the initial value shown in Figure 2.2. This suggests the higher voltage for LC-1 arises, at least initially, from the inherently higher resistivity of the GNP material from which it was fabricated. As discussed later, the increase in voltage for LC-1 that occurs during the electrolysis

FIGURE 3.2. Variation of ΔV with Time During Electrolysis in STP Tests at 1 A/cm² and 0.5 A/cm². (ΔV is the difference in cell voltage for the circuit containing the GNP anode and the circuit containing the standard anode.)

tests may result from electrically driven changes in the composition of the interface or within the anode itself.

It is not completely clear why the resistivity of LC-1 was greater than the standard anodes since the chemical compositions of LC-1 and the standard anodes (ignoring the grain size differences) were very similar (Table 2.1). A possible explanation is that liquid phase sintering is required to achieve adequate connectivity of the metal phase. The fabrication methods used to prepare the standard anodes include a sintering step at a temperature above the melting point of the Cu-Ni alloy phase, while the GNP anodes were sintered below the melting temperature.

Since it was undesirable to have an anode with high resistivity material, it was decided to modify the fabrication procedures to boost conductivity. In particular, the fabrication parameters were changed to give more metal in the cermet anode. This was done despite the fact that LC-1 had an *apparent* chemical composition very close to the standard anodes.^(a) As shown in Table 2.1, the changes in fabrication procedures were successful. Sint#10, prepared using the new procedures, had a metal content of 28% by volume, compared to 13% for Sint#3 prepared with the original procedure.

Despite the greater amount of metal in LC-9, LC-11, and LC-12, these anodes gave a large ΔV similar to LC-1 at the start of the electrolysis, as shown in Figure 3.2. In fact, as shown in Figure 3.3, all four GNP anodes appear to exhibit behavior consistent with Ohm's Law, *assuming a similar resistivity for the four anodes*. Resistivity measurements made on Sint#10 gave very low values, on the order of 0.0005 ohm cm.^(b) For the anodes

-
- (a) The compositions shown in Table 2.1 were obtained with EDS and limited to the technique's sensitivity. Minor amounts of metal phase along grain boundaries, that might explain the difference in conductivity between the standard anodes and LC-1, for example, may be undetectable.
- (b) The fact that this value is three orders of magnitude lower than that for Sint#3 suggests that (approximately) doubling the metal content was enough to achieve connectivity of the metal phase. This explanation is not proven but is offered in line with the previous explanation for the higher resistivity of LC-1.

FIGURE 3.3. Relationship Between the *Initial* ΔV and Current Density in the STP Tests

tested in these studies at 1 A/cm^2 , this corresponds to a ΔV equal to about 0.001 V, or far less than that required to explain the observed value. Clearly, the initial voltage drop for these anodes did not arise from the original composition but from some change that occurred between the time the anode was prepared and the first measurement made during electrolysis. One possibility is that a resistive reaction layer is formed, either by oxidation during heatup of the anode just prior to inserting it into the electrolyte or during the very early stages of electrolysis. The gradual reduction in ΔV may be due to a slow degradation of this layer either by influx of electrolyte, dissolution or some other chemical reaction. Some of the results of microscopic analysis that are discussed in Section 3.3.2 appear to support this possibility.

(a) Standard Anode STD-11

2 mm

(b) GNP Anode LC-1

FIGURE 3.4. Comparison at 6.5X Magnification of a) Standard Anode STD-11 and b) GNP Anode LC-1 after Electrolysis at 1 A/cm^2 for 6 h.

(a) Standard Anode STD-12

(b) GNP Anode LC-9

FIGURE 3.5. Comparison at 6.5X Magnification of a) Standard Anode STD-12 and b) GNP Anode LC-9 after Electrolysis at 1 A/cm^2 for 6 h.

(a) Standard Anode STD-13

(b) GNP Anode LC-12

FIGURE 3.6. Comparison at 6.5X Magnification of a) Standard Anode STD-13 and b) GNP Anode LC-12 after Electrolysis at 1 A/cm^2 for 6 h.

(a) Standard Anode STD-14

2 mm

(b) GNP Anode LC-11

FIGURE 3.7. Comparison at 6.5X Magnification of a) Standard Anode STD-14 and b) GNP Anode LC-11 after Electrolysis at 0.5 A/cm^2 for 6 h.

(a) Standard Anode STD-11

80 μm

(b) GNP Anode LC-1

FIGURE 3.8. Comparison at 250X Magnification of a) Standard Anode STD-11 and b) GNP Anode LC-1 after Electrolysis at 1 A/cm^2 for 6 h.

(a) Standard Anode STD-12

80 μm

(b) GNP Anode LC-9

FIGURE 3.9. Comparison at 250X Magnification of a) Standard Anode STD-12 and b) GNP Anode LC-9 after Electrolysis at 1 A/cm² for 6 h.

(a) Standard Anode STD-13

80 μm

(b) GNP Anode LC-12

FIGURE 3.10. Comparison at 250X Magnification of a) Standard Anode STD-13 and b) GNP Anode LC-12 after Electrolysis at 1 A/cm^2 for 6 h.

(a) Standard Anode STD-14

80 μm

(b) GNP Anode LC-11

FIGURE 3.11. Comparison at 250X Magnification of a) Standard Anode STD-14 and b) GNP Anode LC-11 after Electrolysis at 0.5 A/cm^2 for 6 h.

3.3.2 Microscopic Analysis

Optical micrographs of the four GNP anodes that were tested in electrolysis cells are compared to micrographs of the standard anodes (that were tested in parallel with the GNP anodes) in Figures 3.4 through 3.11. All of the anodes are shown at 6.5X magnification and a portion of the surface (that was exposed to electrolyte) of each anode is shown at 250X magnification. In all cases, the standard anode behaved similarly to previous tests, showing very little, if any, degradation. Some slight amount of Cu metal phase may be lost right near the surface ($<10\text{ }\mu\text{m}$) but the reaction is considered negligible in this study. Since the standard anodes performed well and reproducibly in all of these tests, it was concluded that their results could be used for comparison with the results obtained for the GNP anodes. No serious upsets or anomalies in cell conditions appeared to occur during any of the tests.

In contrast to the standard anodes, the GNP anodes exhibited severe degradation as shown in Figures 3.4 through 3.11. The degradation was characterized by (a) severe bloating of the cermet body, (b) compositional changes including formation of reaction products, (c) increase in porosity, and (d) the ingress of electrolyte components into the cermet body.

3.3.3 Bloating

As shown in Figures 3.4 through 3.7, the GNP anodes bloated during electrolysis, unlike the standard anodes which retained much of their original shape. The change in bulk geometry of the GNP anodes was not quantified, however, because it was almost impossible to determine the original dimensions of anodes from the post-test micrographs. Much of the quantified information, therefore, was derived from the compositional and microstructural changes discussed in Sections 3.3.4 through 3.3.6.

3.3.4 Compositional Changes

Various changes in composition of the GNP anodes occurred during electrolysis. Some of these can be observed in Figures 3.8 through 3.11, which show a portion of the surface region of the anodes that was exposed to the electrolyte. In each figure, the GNP anode is shown with the standard anode that was run in parallel in the same experiment. One of the main observations

FIGURE 3.12. Variation in Thickness of Metal-Depleted Region for Electrolyzed Anodes as a Function of Current Density

from these micrographs is that the metallic phase is depleted in the surface region for all of the anodes. To see if there was any correlation between the thickness of the metal-depleted region developed after the 6-h test and cell conditions, particularly the current density, the plot shown in Figure 3.12 was developed. As shown, the thickness of the layer may increase with current density, although the spread of data at 1 A/cm² makes this conclusion tenuous. It is possible that the metal-depleted region was formed largely before electrolysis, perhaps even before the electrode was inserted into the electrolyte, i.e., by oxidation during heatup as the electrode was being lowered into the cell. Under these circumstances the thickness of the layer would be expected to vary somewhat from test to test performed under the same conditions. This explanation is also consistent with the initial ΔV values for anodes LC-9, LC-11, and LC-12. The preformed layer may be very resistive, giving rise to the initial ΔV . Over longer times in the cell, the layer becomes more porous

and saturated with molten electrolyte, with an accompanying increase in conductivity. This might explain the observed decrease in ΔV with time during the course of the 6-h tests.

Other changes in the composition of the GNP anodes also occurred during the 6-h tests. Displaying micrographs of all of these changes proved to be difficult, however, so they are summarized schematically in Figure 3.13.^(a) The GNP anodes appeared to become laminated with reaction products of varying compositions. Interestingly, many of these reaction products have been found on the standard anodes also, but only after electrolysis for extended periods of time or under conditions where failure occurred.

Very near the surface ($<10\ \mu\text{m}$) of the anodes, a thin layer, rich in aluminum content, formed. Previous work at PNL (Windisch and Stice 1991a) suggested that this layer may be a solid solution formed by the reaction of the spinel phase and Al-containing moieties in the electrolyte. Under the Al-rich layer was an approximately $100\text{-}\mu\text{m}$ -thick layer with no metal phase and composed mainly of spinel (the metal-depleted layer). The presence of mostly spinel in reaction layers on the cermet anodes was documented by Alcoa Laboratories (Weyand et al. 1986) and by PNL in their Prototype Anode Test (Strachan et al. 1990). As a result of studies in FY 1990 (Windisch and Stice 1991a), PNL proposed that the spinel phase remained behind, possibly protected by the Al-rich reaction product, as the NiO "fell out" of the ceramic matrix after prolonged electrolysis and agitation by the gas bubbles being generated.

Under the metal-depleted layer, were two other layers also containing spinel. The layer closer to the electrolyte also contained copper oxide (mostly Cu_2O), while the layer above it contained almost-pure Cu metal. The presence of Cu_2O as a reaction phase was identified previously in the Prototype Anode Test (Strachan et al. 1990). It is believed that, despite the

(a) There were some variations in the dimensions of the layers from anode to anode similar to the thicknesses of the metal-depleted layer in Figure 3.12. As indicated, these dimensions appeared to bear no relationship to the electrolysis conditions in the studies reported here. Figure 3.13 simply gives a schematic of the different layers observed on the anodes.

FIGURE 3.13. Schematic of Layers of Various Compositions in GNP Anodes after Electrolysis

production of voluminous amounts of oxygen gas during electrolysis, redox conditions within the electrode (or thermal stability considerations) favor Cu_2O over CuO . The formation of pure Cu metal from the original Cu-Ni alloy has also been observed in the subsurface regions of used anodes (Windisch and Stice 1991a) and was explained by the selective oxidation of Ni from the alloy phase.

Clearly, much of the chemistry previously observed on standard anodes after extended periods of electrolysis was reproduced on the GNP anodes in these short-term tests. The reactions on the GNP anodes were more severe; however, the chemistry was similar. This suggests that, while the kinetics may be very different, the information on the *types of chemical reactions* gained in these tests is directly applicable to standard anode behavior.

Future development of any new cermet materials might consider some evaluation of fine-grain microstructure materials as an approach to accelerated screening. Distinguishing a set of *good* anodes such as the standard anodes tested here is almost impossible in a 6-h test with the cell operating under optimal conditions. Conducting an accelerated, fine-grain microstructure test, however, would demonstrate the types of reaction products expected. This could help streamline subsequent larger-scale experiments over much longer periods.

In addition to the EDS measurements reported above, area percentage data were also collected using image analysis. These data supplemented the EDS results in helping to *quantify* compositional changes in different regions of the electrolyzed anodes. An area percentage is a percentage of the area of an image of a sample with a certain "grayness." Different shades of gray are correlated with different phases in the sample. In this work, at least three phases were distinguished in all tested anodes: an oxide phase (gray), a metallic phase (white) and porosity (black). Different shades of gray (reflecting the different oxide phases) were distinguishable in some samples but not in all; this is because the microstructure is small and the components uniformly distributed. Consequently, for the purposes of comparison in this work, the areas of the various oxide phases were combined as a "total oxide phase."

The area percentages of the various phases in the gray-scale images for *electrolyzed* anodes are given in Table 3.2. Data are given for three regions of each anode: the bottom (area in the center of the anode but near its surface, i.e. at the electrode/electrolyte interface), the corner (area near the corner of the anode at the electrode/electrolyte interface), and the center (area near the very center of the anode or, for these anodes, about 1.5 cm above the electrode/electrolyte interface).

The data in Table 3.2 suggest some important relationships between the chemical transformations and the types of anodes and conditions of electrolysis. First, the standard anodes all behaved similarly under the various test conditions. Measurements on STD-12, 13 and 14 were so similar that average values are given for both the bottom and center positions. (Corner positions

TABLE 3.2. Area Percentages of Phases Using Image Analysis

Location	Anode	Density	Porosity	Metal	Oxide
Bottom	LC-1	1 A/cm ²	41.2	0	58.8
	LC-9	1	15.6	0	84.4
	LC-12	1	24.1	0	75.9
	LC-11	0.5	26.1	0	73.9
	STD-12-14 ^(a)	1	4.3	11.9	83.8
	STD-11	0.5	4.8	10.7	84.5
Center	LC-1	1 A/cm ²	12.9	20.7	66.4
	LC-9	1	16.9	23.2	59.9
	LC-12	1	7.3	27	65.7
	LC 11	0.5	3.8	27	69.2
	STD-12-14	1	2.4	14.6	83.0
	STD-11	0.5	4.8	10.7	77.4
Corner	LC-1	1 A/cm ²	40.9	0	59.1
	LC-9	1	20.1	0	79.9
	LC-12	1	23.0	0	77.0
	LC-11	0.5	12.9	0	87.1

(a) Average values given.

were not studied for the standard anodes because they exhibited the same structure as the bottom sections.) As shown in Table 3.2, the standard anodes generally showed significantly less metal loss and less porosity than the GNP anodes. Differences in these parameters between the standard anodes run at 1 A/cm² and the standard anode run at 0.5 A/cm² were not significant, indicating that the test conditions were not severe enough to distinguish current density effects on these parameters for the standard anodes alone.

The GNP anodes showed no evidence of metal content in the bottom and corner regions, consistent with the EDS analysis reported above. Consequently, metal content in the surface region could not be used to compare the extent of anode degradation for the GNP anodes. Metal content in the center region was higher for the GNP anodes than for the standard anodes. This was

expected for LC-9, LC-11, and LC-12 since they were fabricated to contain more metal. LC-1 should have contained the same amount of metal as the standard anodes (13%) but did not, according to the one measurement taken. The reason for this latter result is unclear at this time, although some redistribution of metal deep within the cermet would not be surprising given the extensive degradation of the anode (Figure 3.4).

Porosities for all of the GNP anodes were higher than the standard anodes in these post-test analyses. Moreover, the porosities appeared to show some, if slight, dependence on the cell conditions. At the center position (where the metal content is nonzero) the porosity and metal content appear (although not exactly) inversely related. This suggests that the porosity may be a good way to quantify the extent of GNP anode degradation. (The porosities of the GNP anodes were all similar at the start of the tests.) For this reason, the porosities of the GNP anodes and their variation with cell conditions are the focus of the next section.

3.3.5 Porosity

Binary images showing the porosities of all of the anodes tested are shown in Figures 3.14 through 3.21 along with the gray-scale images from which they were derived. In the binary images, the pores are shown as black and all other phases are white. (The region outside of the anode is also black but this area may be ignored.) Comparing the GNP anodes with the standard anodes, it is clear that the porosities of the GNP anodes were greater, extended to deeper locations, and were generally coarser than for the standard anodes. Plotting the porosities in Table 3.2 as a function of current density also suggests^(a) some interesting trends.

As shown in Figures 3.22 through 3.24, the porosities (at all three locations) appear to increase with current density. The most precise

(a) Since only limited data were available in this work (only two current densities were studied with only one measurement at 0.5 A/cm^2), interpretations should be made very cautiously. Data at 0 A/cm^2 were the porosity values for the non-electrolyzed GNP anodes (Sint#3 and Sint#10).

Grey scale image

100 μm

Binary image of porosity phase

FIGURE 3.14. Porosity of Bottom Region of Standard Anode STD-11 after Electrolysis at 1 A/cm^2 for 6 h

Grey scale image

100 μm

Binary image of porosity phase

FIGURE 3.15. Porosity of Bottom Region of Standard Anode STD-12 after Electrolysis at 1 A/cm^2 for 6 h

Grey scale image

100 μm

Binary image of porosity phase

FIGURE 3.16. Porosity of Bottom Region of Standard Anode STD-1.3 after Electrolysis at 1 A/cm^2 for 6 h

Grey scale image

100 μm

Binary image of porosity phase

FIGURE 3.17. Porosity of Bottom Region of Standard Anode STD-14 after Electrolysis at 0.5 A/cm^2 for 6 h

Grey scale image

100 μm

Binary image of porosity phase

FIGURE 3.18. Porosity of Bottom Region of GNP Anode LC-1 after Electrolysis at 1 A/cm^2 for 6 h

Grey scale image

100 μm

Binary image of porosity phase

FIGURE 3.19. Porosity of Bottom Region of GNP Anode LC-9 after Electrolysis at 1 A/cm^2 for 6 h

Grey scale image

100 μm

Binary image of porosity phase

FIGURE 3.20. Porosity of Bottom Region of GNP Anode LC-12 after Electrolysis at 1 A/cm^2 for 6 h

Grey scale image

100 μm

Binary image of porosity phase

FIGURE 3.21. Porosity of Bottom Region of GNP Anode LC-11 after Electrolysis at 0.5 A/cm^2 for 6 h

FIGURE 3.22. Relationship Between Current Density and Porosity in Corner Sections of Electrolyzed GNP Anodes

correlation appears for the corner sections where the trend for LC-9, LC-11, and LC-12 is almost linear. LC-1, which has a different chemical composition, shows a similar, although somewhat stronger, dependence (with respect to the value at 0 A/cm², in this case Sint#3). The variation of porosity in the bottom and center sections is consistent with the variation in the corner region (although perhaps not linear), despite being much less precise. The greater spread of data for the bottom and center regions may result from two factors: 1) the larger influence of other parameters, such as the effects of pull-outs in the center region where the porosity is generally smaller, and 2) the possible effects of a preformed reaction layer in the bottom region. (The possibility of a preformed reaction layer was discussed in Section 3.3.1.)

All of the results from porosity measurements are summarized in the bar graph in Figure 3.25. Anode LC-1 exhibited the most degradation as indicated by the increase in porosity. This is attributed to the different microstructure and composition of anode LC-1, but it is unclear, at this point, exactly

FIGURE 3.23. Relationship Between Current Density and Porosity in Bottom Sections of Electrolyzed GNP Anodes

what parameters contributed to the much poorer performance of this GNP anode. The dramatic increase in porosity of all of the GNP anodes, taken together with the compositional changes discussed earlier, indicate the presence of some mode of failure that is absent or much reduced in larger-grained anodes. Some clues to the cause of this failure are given in Figure 3.26, which shows the distribution of the element aluminum within anode LC-9 after electrolysis. An SEM micrograph of the bottom region is shown in Figure 3.26(a) and an aluminum map of this same region is shown in Figure 3.26(b). An aluminum map for the same anode, but at a position much deeper (about 1.5 cm) in the sample, is shown in Figure 3.26(c).

Two principal observations can be made in Figure 3.26. First, the electrolyte (which is the principal source of elemental aluminum) penetrates the anode, probably along grain boundaries. Moreover, the penetration proceeds to depths well within the anode body. Some of the compositional changes of the phases, even at locations in the center of the anodes (as reported in

FIGURE 3.24. Relationship Between Current Density and Porosity in Center Sections of Electrolyzed GNP Anodes

Section 3.3.4), may, therefore, arise from to interactions with the electrolyte. The second observation that can be made in Figure 3.26 is that the reaction layer at the surface of the anode is rich in aluminum. This result is consistent with the formation of an aluminum-rich reaction product similar to that proposed in a previous PNL report (Windisch and Stice 1991a) and discussed in Section 3.3.4 of this report. This layer appears to form "over" the spinel phase, and, at least for larger-grain versions of the cermet anode, may slow the dissolution of the spinel phase to "acceptable" levels.

3.3.6 Effects of Microstructure

The principal objective of this work was to determine the effects of microstructure, in particular the grain size, on the durability of cermet inert anodes. Consequently, it would be useful to plot some parameter that quantifies durability or the extent of corrosion as a function of microstructure and, if possible, cell conditions such as current density. The limitation to this approach for the present work is that very few data points were

FIGURE 3.25. Bar Graph Summarizing Porosities Measured at Various Locations for Electrolyzed GNP Anodes

obtained, so any plots must be interpreted with caution. Moreover, few compositional or morphological parameters showed an *unequivocal* correlation with current density, suggesting that the conditions were *very severe* for all of the GNP anodes and conditions tested.

Despite the above limitations and concerns, however, three important observations can be made. First, the GNP anodes showed significantly greater deterioration as a result of electrolysis than the standard anodes. Second, bearing in mind that some compositional differences existed between the GNP anodes and the standard anodes, it appears that the principal mode of attack of the cermet anodes is along grain boundaries. A finer-grain microstructure means more grain boundaries which, in turn, may promote more extensive interaction between the electrolyte and the cermet material.^(a) Finally, of

-
- (a) The effects of composition are very important so this conclusion is made with some caution. Chemical moieties (impurities) along grain boundaries are known to influence grain boundary attack in metals and ceramics, and it is quite possible that these species are different in the GNP anodes since they were made using different procedures and from different starting materials.

**(a) SEM of Bottom
of LC-9**

200 μm

**(b) Al Map of Bottom
of LC-9**

**(c) Al Map of Interior
of LC-9**

FIGURE 3.26. SEM Micrograph and EDS Elemental Aluminum Distribution Maps for GNP Anode LC-9 after Electrolysis a) SEM Micrograph of Bottom Region b) EDS Elemental Aluminum Distribution Map for Bottom Region and c) EDS Elemental Aluminum Distribution Map for Interior Region

all the parameters related to anode degradation that were examined in this work, porosity seems to show the most meaningful (although still "noisy") relationship to the current density at which the anode was tested. From previous work (Strachan et al. 1988), it was anticipated that increasing the current density would accelerate corrosion, and this trend is consistent with measurements of porosity at various locations within the GNP anodes for the range of conditions studied. In light of this last observation, it is useful to examine the relationships (again with some reservation because of the limited data) between the porosity measurements and anode grain size.

Figures 3.27 and 3.28 show the relationship between the grain size (quantified by the diameter of the metal phase, assuming spherical particles) and the porosity of the anodes measured after electrolysis at a center position and at a corner position, respectively. Data are shown for both of the current densities tested. The figures suggest that the porosity of the cermet anodes increases dramatically for smaller-grain microstructures. Also, the increase in porosity appears to be greater at higher current densities. These data suggest that an optimal microstructure for the cermet inert anodes would contain grains significantly larger than the GNP anodes and/or be fabricated to minimize attack along the grain boundaries, provided, of course, that porosity is indicative of the extent of anode degradation and compositional differences between the various anodes (including differences in the bulk composition of LC-1 and the other GNP anodes, and differences in the composition of grain boundary regions) play a minor role.

The current standard anodes may, in fact, already be optimized with regard to grain size. Comparison testing on even larger-grained analogues would appear to be more suited to larger-cell, longer-term testing. Significant fundamental research is required, however, to develop strategies for arresting grain boundaries attack. It still remains to be determined how the electrolyte is transported along the grain boundaries, what chemical species are involved in the transport, and what role - if any - various grain boundary components (or impurities) have on the corrosion rate. With knowledge provided by fundamental work, it might be possible, by a comparison of the

FIGURE 3.27. Plot of Grain Size Versus Porosity in the Center of Anodes Electrolyzed at (a) 1 A/cm^2 and (b) 0.5 A/cm^2 . (Grain size is taken as the diameter of the metal phase envisioned as equivalent spheres.)

mechanisms for the cermet anode system with other well-studied systems that: - undergo intergranular attack, to develop new compositions or bath additives or to define different operational conditions that adequately reduce the extent of this type of corrosion.

FIGURE 3.28. Plot of Grain Size Versus Porosity in the Corner of Anodes Electrolyzed at (a) 1 A/cm^2 and (b) 0.5 A/cm^2 . (Grain size is taken as the diameter of the metal phase envisioned as equivalent spheres.)

FIGURE 3. Plot of Grain Size Versus Porosity in the Corner of Anneals
 Electrolyzed at 10 V/cm and 10 V/cm. Grain
 size is taken as the diameter of the metal phase or isostatic
 and equivalent spheres.

4.0 CONCLUSIONS

The GNP method was used successfully to make cermet inert anodes with much finer-grain microstructures than the standard cermet anodes. Some of the GNP anodes also differed from the cermet anodes in chemical composition. These results indicate that the GNP method may be used to vary both compositional and microstructural parameters.

Additional work is required to tune the fabrication parameters so as to achieve, reproducibly, a chemical composition of the cermet phases that is more similar to that of the standard anodes (with only the scale of microstructures different). Only in this way can the effects of microstructure scale be separated unambiguously from the effects of composition of the various cermet phases. Compositional parameters, e.g., percent metal phase, can also be varied to determine their effects.

Electrolysis testing of the GNP anodes in the STP cells caused severe degradation of the GNP anodes compared with the standard anodes. Post-mortem analysis of the anodes showed that the mode of attack was along grain boundaries, and when porosity changes were used to quantify degradation, that the amount of attack increased with increasing current density and decreasing microstructural grain size. However, these conclusions were based on very few experiments, and further work is required to corroborate and extend (to other current densities and microstructures) the scope of these findings.

The studies conducted to date do, however, confirm the supposition that microstructural parameters affect anode performance. They also suggest certain directions that future research could take. Some suggestions include the following: (1) the GNP procedures could be fine tuned to develop a series of anode microstructures with varying scale but constant compositions, and these anodes could be tested using methods similar to those reported here; (2) GNP procedures could be modified to permit some anodes to be made via liquid-phase metal sintering for comparison with the lower-temperature sintered material; (3) GNP procedures could be changed to permit a range of compositions, e.g., metal phase contents, to be obtained, also for comparison testing; (4) the possibility of extending the GNP approach (or other

approaches) to making coarser-grained microstructures could be explored; and (5) more fundamental studies on the roles of grain boundaries in anode corrosion could be initiated. Research to understand better the grain boundary chemistry of the cermet anodes could lead to improvements in microstructure composition and performance, similar to the progress that has been made in the area of intergranular corrosion of metals over the past several years.

5.0 REFERENCES

Chick, L. A., L. R. Peterson, G. D. Maupin, J. L. Bates, L. E. Thomas, and G. J. Exarhos. 1990. Materials Letters, Vol. 10, No. 1, pp. 6-12.

Strachan, D. M., O. H. Koski, S. C. Marschman, C. H. Schilling, and C. F. Windisch Jr. 1988. Fiscal Year 1987 Annual Report for the Inert Electrodes Program. PNL-6746, Pacific Northwest Laboratory, Richland, Washington.

Strachan, D. M., C. F. Windisch Jr., O. H. Koski, L. G. Morgan, R. D. Pederson, N. E. Richards, and A. T. Tabereaux. 1990. Results from Electrolysis Test of a Prototype Inert Anode. PNL-7345, Pacific Northwest Laboratory, Richland, Washington.

Weyand, J. D., D. H. DeYoung, S. P. Ray, G. P. Tarcy, and F. W. Baker. 1986. Inert Anodes for Aluminum Smelting: Final Technical Report for the Period 1980 September 29 - 1985 September 30. DOE-CONS-40158-20, Alcoa Laboratories, Alcoa Center, Pennsylvania.

Windisch, C. F., Jr., and N. D. Stice. 1991a. Final Report on the Characterization of the Film on Inert Anodes. PNL-7589, Pacific Northwest Laboratory, Richland, Washington.

Windisch, C. F., Jr., and N. D. Stice. 1991b. Report on the Source of the Electrochemical Impedance on Cermet Inert Anodes. PNL-7629, Pacific Northwest Laboratory, Richland, Washington.

DISTRIBUTION

No. of
Copies

No. of
Copies

OFFSITE

	M. J. McMonigle U.S. Department of Energy Office of Industrial Programs Forrestal Building Washington, DC 20585	J. A. Barclay U.S. Bureau of Mines 2401 "E" Street N.W. Washington, DC 20241
	P. H. Salmon-Cox U.S. Department of Energy Office of Industrial Programs Forrestal Building Washington, DC 20585	H. Robert Baumgartner Ceramics Division Alcoa Laboratories Alcoa Center, PA 15069
12	DOE Office of Scientific and Technical Information	T. R. Beck Electrochemical Technology Corp. 1601 Dexter Avenue Seattle, WA 98109
	C. Anderson Columbia Aluminum Co. 85 John Day Dam Road Goldendale, WA 98620	S. Berwagan Bonneville Power Administration P.O. Box 3621 K Portland, OR 97208
	J. V. Anderson WCVE3 EG&G Idaho, Inc. Idaho Falls, ID 83415	T. M. Besmann Metals and Ceramics Division Oak Ridge National Laboratory P.O. Box X, Bldg. 4515 Oak Ridge, TN 37831-6063
	D. Auburg Bonneville Power Administration P.O. Box 3621, PDX 97208 Portland, OR 97208	K. A. Blakely President Advanced Refractory Technologies, Inc. 699 Hertel Ave. Buffalo, NY 14207
	F. W. Baker Ceramics Division Alcoa Laboratories Alcoa Center, PA 15069	M. H. Blenk Du Pont P.O. Box 787 Niagara Falls, NY 14302
	M. Baltzell Eastalco Aluminum Company Alumax, Inc. 5601 Manor Woods Frederick, MD 21701	L. G. Boxall Martin Marietta Laboratories 1450 South Rolling Baltimore, MD 21227

No. of
Copies

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

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

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

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

A. J. Caputo
Development Division
Oak Ridge Y-12 Plant
Building 9202 MS-8095
Oak Ridge, TN 37831-8095

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

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

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

No. of
Copies

Business Expansion
Division Library
Washington State Dept of Trade
Business Expansion Library
2001 6th Avenue # 2700
Seattle, WA 98121-2522

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

J. V. Day
Kaiser Aluminum and Chemical
Corp
E2111 Hawthorne Road
Mead, WA 99021

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

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

C. W. Doerr
The Stackpole Corporation
Cermag Division
201 Stackpole Street
St. Marys, PA 15847

T. Dwonch
Snake River District
BPA
101 W. Poplar
Walla Walla, WA 99362

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

No. of
Copies

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

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

B. G. Epstein
A. D. Little, Inc.
955 Lenfant Plaza SW 4200
Washington, DC 20024-2119

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

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

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

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

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

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

No. of
Copies

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

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

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

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

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

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

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

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

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

No. of
Copies

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

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

F. R. Huettig
Advanced Magnetics, Inc.
45 Corey Lane
Mendham, NJ 07945

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

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

S. H. Jan
Tennessee Valley Authority
R&D Division - MR 3A
Chattanooga, TN 37401

N. Jarrett
149 Jefferson Avenue
New Kensington, PA 15068

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

M. H. Johnson
Alcoa Wenatchee Works
P.O. Box 1031
Elizabethton, TN 37643

No. of
Copies

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

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

R. Keller
RD 3 Roundtop Road
Export, PA 15632

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

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

R. A. Landy
Director of Research
North American Refractories
Co.
3127 Research Dr.
State College, PA 16801

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

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

No. of
Copies

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

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

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

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

W. Long
Building B815
Dow Chemical
Freeport, Texas 77541

A. G. Longmuir
Kaiser Aluminum and Chemical
Corp.
P.O. Box 877
Pleasanton, CA 94566

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

W. N. Maclay
Koppers Company, Inc.
1005 William Pitt Way
Pittsburgh, PA 15238-1336

J. C. McCloskey
Ten Mile River Associates
296 Mt. Hope Street
North Attleboro, MA 02760

No. of
Copies

S. C. Manaktala
Manager of Technology
Reduction Division
Kaiser Aluminum and Chemical
Corp
300 Lakeside Drive
Oakland, CA 94643

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

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

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

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

H. Mortensen
R. Palika
Cercom, Inc.
P.O. Box 70
Vista, CA 92083

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

No. of
Copies

P. Ness
Washington State Dept of Trade
and Economic Development
2001 6th Avenue #2600
Seattle, WA 98121-2522

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

T. Payne
Columbia Falls Aluminum Co.
Columbia Falls, MT

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

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

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

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

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

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

No. of
Copies

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

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

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

R. C. Rohwedder
3028 Ohio Street
Longview, WAD. R. Sadoway
MIT
Room 8-109
77 Massachusetts Avenue
Cambridge, MA 02139

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

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

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

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

No. of
Copies

Brian Spector
Pace Consultants
4848 Loop Central Drive
Houston, TX 77081

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

Dr. Richard M. Spriggs
Office of the Director
Center for Advanced
Ceramic Technology
Alfred University
Alfred, NY 14802

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

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

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

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

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

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

No. of
Copies

S. Thomson
General Manager
Klickitat PUD
1313 S. Columbus
Goldendale, WA 98620

R. Unger
Merner Research
P.O. Box 248
Ridgewood, NJ 07451A. Vinnard
Bonneville Power
Administration (KWI)
P.O. Box 3621
Portland, OR 97208

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

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

J. D. Weyand
EG&G Idaho, Inc.
Idaho Falls, ID 83415

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

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

FOREIGN

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

No. of
Copies

H. Connor
Group Licensing Controller
Johnson Matthey, plc
New Garden House
78 Hatton Garden
London EC1N 8JP ENGLAND

L. Dion
Alcan International Limited
C.P. 6090
Montreal, Quebec
CANADA, H3C 3H2

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

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

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

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

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

No. of
Copies

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

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

Dr. Eric Frazer
CSIRO Australia
Division of Mineral Products
339 Williamstown Road
P.O. Box 124
Port Melbourne, Vic 3207

ONSITE

DOE Field Office, Richland

R. B. Goranson

25 Pacific Northwest Laboratory

M. Clement
N. C. Davis
D. K. Hilliard
G. L. McVay
N. L. Moore
L. G. Morgan
C. H. Schilling
D. M. Strachan
R. E. Westerman
C. F. Windisch (10)
Publishing Coordination
Technical Report Files (5)