SELECTION AND TESTING OF INERT ANODE MATERIALS FOR HALL CELLS

Alan D. McLeod, Jean-Marc Lihrmann, John S. Haggerty, and Donald R. Sadoway,

Department of Materials Science and Engineering,
Massachusetts Institute of Technology,
Cambridge, Massachusetts, 02139

A new set of criteria for Hall cell anode materials is presented. Fundamental thermodynamic data are used to estimate how well a variety of oxides will satisfy these criteria in the context of the total environment of an operating industrial cell. In addition, the results of tests of candidate anode materials performed in this laboratory are presented.

INTRODUCTION

While the current efficiency in modern Hall – Héroult cells exceeds 90% the voltage efficiency is less than 30%. In large measure the latter is a consequence of the present choice of electrode materials, which imposes severe limitations on cell design, most notably the need to separate the electrodes by a spacing so great that more than 40% of the total cell voltage is associated with the so – called iR drop across the electrolyte. The discovery of materials for an inert anode, wettable cathode, and inert sidewall would pave the way for radical innovation in cell design and operation with attendant improvements in productivity. This paper will be restricted to the discussion of inert anode materials.

The search for inert anode materials has proved to be one of the most difficult challenges for modern materials science. While a variety of formulations has been proposed and numerous patents have been granted (1) no material has proven to be fully satisfactory. Indeed, it may well be that there is no material that can meet the requirements of an industrial cell. At least, this seems to be the conclusion of all previous research which was directed to find "the inert anode material". It is the opinion of the authors that a totally different approach must be adopted, i.e., not to look for "the inert anode material" but rather to consider the entire cell in the context of a dynamic materials system. The purpose of this paper is then to state clearly the criteria of selection and to pose the problem in the light of the above.

Until recently, materials used for inert anode formulations were selected from those oxides that have low solubilities in cryolite (Na_3AlF_6), for example : Fe_2O_3, SnO_2, and Cr_2O_3. [6] Electrical conductivity is enhanced by doping with oxide additions to the host materials or by the presence of a distinct metal phase to form a cermet. The disadvantage in such cases is that the host is selected without consideration of all the criteria and on the basis of a relatively small and frequently inaccurate data base. By consideration of other fundamental materials property data, in particular thermodynamic data, it is possible to establish an improved rationale for materials selection. Laboratory testing is necessary to confirm that candidate materials behave according to expectations.

MATERIALS SELECTION

In selecting candidate anode materials one must consider as nearly as possible how that material will behave in its total environment. In an operating Hall cell this environment is not homogeneous. While the electrolyte consists of cryolite (Na_3AlF_6) – AlF_3 – CaF_2 – Al_2O_3 there are severe gradients in chemical potential across the interelectrode gap. In the vicinity of the inert anode the melt is highly oxidizing due to the evolution of pure oxygen at pressures exceeding one atmosphere. Near the cathode the melt is highly reducing due to the presence of dissolved elemental aluminum. All the while as the cell operates electrical current is passing at current densities near 1 A/cm^2. Given this complex set of conditions it should be apparent that consideration of chemical dissolution of a candidate material in pure cryolite or even cryolite containing dissolved Al_2O_3 cannot alone serve as the basis for materials selection.

For example, the interaction of the candidate material with the aluminum dissolved in the electrolyte must be considered. The aluminum may reduce the metal oxide allowing the metal to itself dissolve in the electrolyte. Alternatively, a metal oxide may dissolve by forming a metal fluoride through an exchange reaction with the electrolyte.

Since cryolite will dissolve most, if not

all, oxides to some extent, one must consider what happens to a metal oxide once it is in solution. The metal can co-deposit with aluminum by electrolytic reduction or dissolve in the molten aluminum cathode following a metallothermic - type displacement reaction. The second new criterion, then, uses the electrochemical series in the Hall cell electrolyte to predict whether or not a metal will co-deposit. The third new criterion considers whether or not elemental aluminum will displace the impurity metal from the electrolyte by chemical reaction.

The diagram shown in Figure 1 can be used as an aid in discussing the concepts behind the proposed selection criteria. Similar to a decision tree, the diagram shows the tests a metal oxide must pass in order to be deemed useful as an anode. The first test considers the exchange reaction between the candidate metal oxide and dissolved aluminum. If aluminum reduces the metal oxide the material fails this test. However, as will be
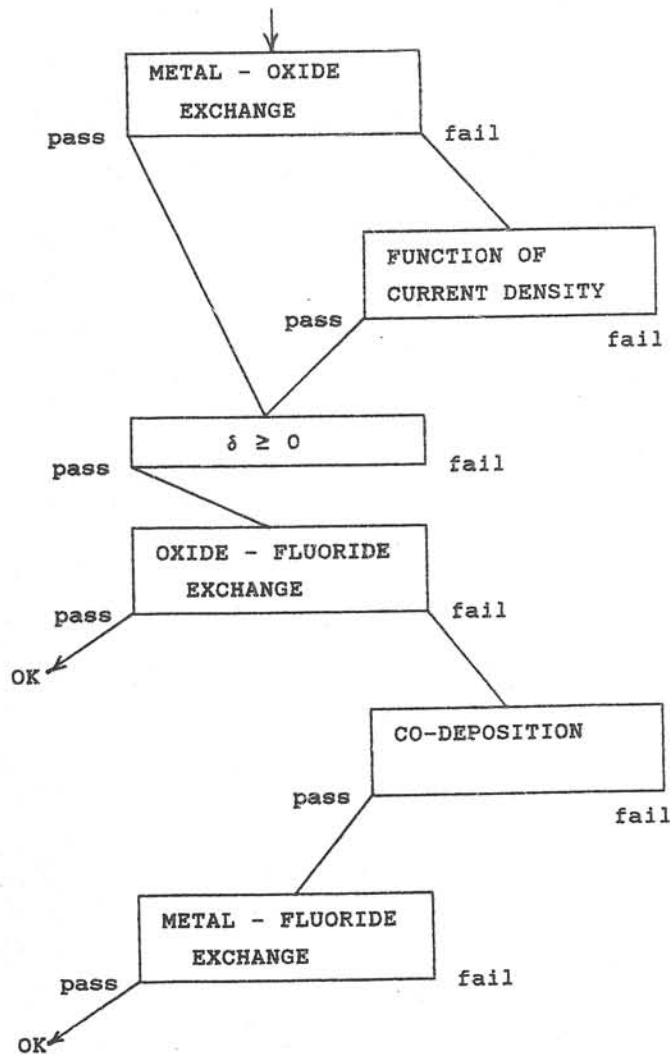
discussed in more detail below, an oxide can be protected from chemical attack by dissolved aluminum by the oxygen evolving on the anode. This oxygen acts to oxidize the dissolved elemental aluminum thereby reducing its concentration in the vicinity of the anode. Thus protected, it can still pass the first test, hence, an alternate route through "function of current density" has been included.

The third and fourth boxes determine if the oxide passes both stages of the second test. The issue here is the chemical dissolution of the metal oxide through the exchange reaction between the oxide and the molten fluorides. The first stage of this test, "$\delta \geq 0$" refers to a condition where the metal changes valence when going into solution. It will be shown that it is undesirable to have the valence of the metal increase as shown by a negative value for δ. An oxide that does not go into solution through the oxide - fluoride exchange process will pass the second stage of this test. An oxide that fails this test should not be dropped from consideration, however. The material could still be acceptable if it can pass both of the last two tests, "co-deposition" and "metal - fluoride exchange". The following discussion will consider each test in turn starting from the top of the diagram. An examination of the applicable thermodynamic data will indicate which oxides will pass which tests. The end result of this examination will be a list of oxides that are acceptable for use as anode materials on the basis of the criteria enumerated in this paper.

Both the metal - metal oxide and metal oxide - metal fluoride reactions can be thought to occur at the anode surface. The former reaction between the anode and dissolved elemental aluminum can be represented by :

$$MeO_{\frac{n}{2}} + \frac{n}{3}Al == \frac{n}{6}Al_2O_3 + Me \qquad (1)$$
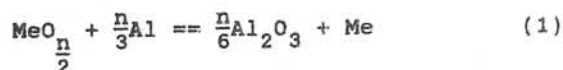
This reaction is also referred to as the "crucible reaction", i.e., would a crucible made of the metal oxide under consideration be acceptable as container of molten aluminum at Hall cell operating temperatures? If aluminum oxide is stabler than the metal oxide of the crucible a reaction will occur consuming the crucible until the melt is exhausted of dissolved aluminum or is saturated with alumina. The free energy change for reaction (1) calculated per mole of metal, Me, at 1300 K is given for various oxides in Table I. All thermodynamic data for this and subsequent analyses have been taken from Barin and Knacke (2,3). Evidently a series of oxides from ZrO_2 to Y_2O_3 will satisfy the first criterion. Their positive ΔG indicates that dissolved aluminum will not reduce the oxide if it is assumed that the activities of dissolved metals are unity. Of course during electrolysis, the anode will be surrounded by a "shroud" of O_2. The

Figure 1. Stages in Materials Selection.

Table I. Free Energy of Reaction for Metal – Oxide Exchange at 1300 K

OXIDE	ΔG_1 (kJ)	OXIDE	ΔG_1 (kJ)	OXIDE	ΔG_1 (kJ)
PbO_2	−829	Ta_2O_5	−303	CeO_2	−30
WO_3	−733	NiO	−301	BaO	−12
Rh_2O_3	−613	CdO	−295	Li_2O	−11
SbO_2	−609	CoO	−284	TiO	−8
SnO_2	−528	FeO	−233	ZrO_2	19
Bi_2O_3	−522	Cr_2O_3	−231	UO_2	22
V_2O_5	−521	ZnO	−229	SrO	31
GeO_2	−507	Cu_2O	−184	MgO	33
WO_2	−482	V_2O_3	−181	BeO	54
Sb_2O_3	−448	K_2O	−165	CaO	72
CuO	−385	SiO_2	−150	La_2O_3	76
Fe_2O_3	−384	B_2O_3	−145	Nd_2O_3	77
Nb_2O_5	−370	MnO	−139	Sm_2O_3	82
PbO	−347	TiO_2	−130	Ce_2O_3	110
VO_2	−330	Na_2O	−124	Sc_2O_3	129
Mn_2O_3	−321	VO	−108	Y_2O_3	132
Ga_2O_3	−304	Ti_2O_3	−48		

Table II. Free Energy of Reaction for Metal Oxide – Metal Fluoride Exchange at 1300 K

OXIDE	ΔG_2 (kJ)	OXIDE	ΔG_2 (kJ)
SrO	−190	Bi_2O_3	33
PbO_2**	−156	Fe_2O_3*	59
Y_2O_3	−119	Nb_2O_5	112
Sc_2O_3	−50	V_2O_3	136
PbO	−47	Mn_2O_3	144
Ti_2O_3	−6	PbO_2	148
CoO	−1	VO_2*	174
MnO	24	VO_2	223
Mn_2O_3*	28	WO_3	255

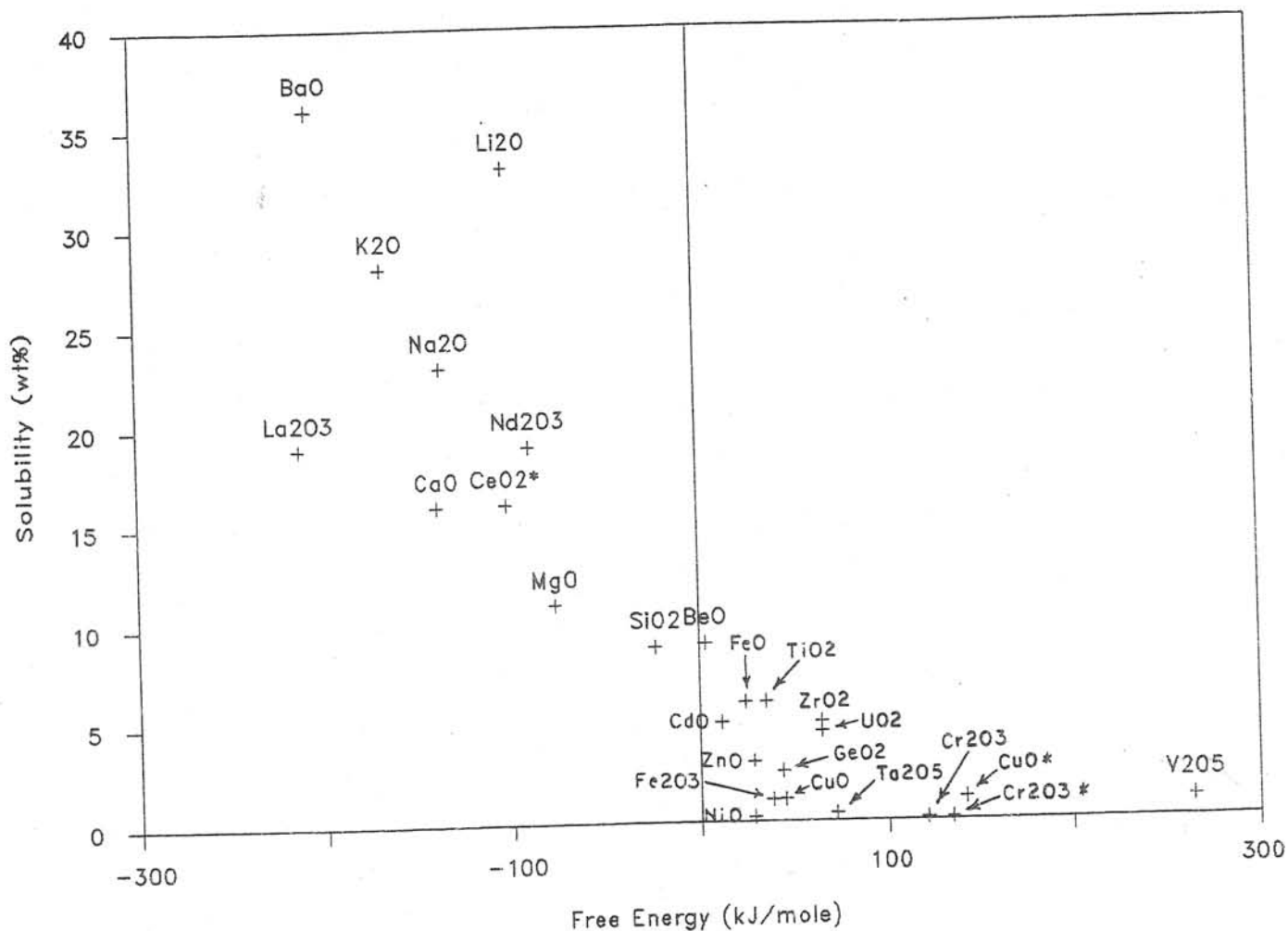Figure 2. Metal Solublity Plotted Against ΔG_2.

resulting high oxygen pressure, P_O, will certainly lower the dissolved metal activity. This effect could move reaction (1) in either direction, depending on the metal valence, n, and the relative metal activities. For this reason some oxides may still satisfy the first criterion due to the activity shift. The importance of Table I is that it indicates that some oxides will be more susceptible to attack than others. It will be seen that the following criteria are more stringent in any case.

The metal oxide - metal fluoride exchange reaction occurring at the anode surface can be described by reaction 2 :

$$MeO_{\frac{n}{2}} + \frac{n-\delta}{3}AlF_3 == MeF_{n-\delta} + \frac{n-\delta}{6}Al_2O_3 + \frac{\delta}{4}O_2 \quad (2)$$
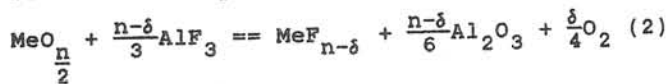
The value of δ is non - zero when the metal oxide changes valence state as it goes into solution. In such cases the thermodynamics of the reaction are influenced by the P_O. When $\delta < 0$, the reaction is forced to the right at higher values of the P_O, clearly not a desirable result. One can argue that ΔG_2 is related to the solubility of the metal

oxide. Evidence of this can be seen in Figure 2 where solubility is plotted against ΔG_2 per mole of Me at 1300 K. The solubility data used in Figure 2 were taken from Table 10.3 in the book by Grjotheim et al. (4). This plot also shows that a positive ΔG_2 is no assurance that a metal oxide will not go into solution but rather indicates only that the metal oxide will dissolve at a reduced activity level. In fact, the values of ΔG_2 are useful primarily to rank oxides in relation to relative reactivities. The values of ΔG_2 for some oxides whose solubilities have not been measured are listed in Table II. The attached "*"'s indicate a condition where $\delta > 1$, "*" meaning $\delta = 1$, and "**" meaning $\delta = 2$. A question arises at this stage as to the importance of the second criterion in comparison with other criteria. If an oxide did not go into solution then it would certainly be acceptable as far as this criterion goes. However, it is safe to assume that all metal oxides will go into solution in varying degrees, the extent depending on the driving force, ΔG_2. Rather, it is better to consider what happens to the oxide once it has dissolved in the electrolyte. The final two criteria consider the behavior of the

dissolved metal at the cathode.

The metal Me can report to the aluminum product through two mechanisms - electrolytic co-deposition or chemical reduction by aluminum itself. Once in the metal, the impurity must either be removed or tolerated. If the metal is not returned to the cell in some form, the contamination of the aluminum product by the metal constitutes consumption of the anode material.

The co-deposition criterion can be employed using the calculated reversible decomposition potential, E°, at 1300 K for the reaction :

$$MeO_{\frac{n}{2}} \Longrightarrow Me + \frac{n}{4}O_2 \qquad (3)$$

This can be calculated using the equation :

$$E_3^\circ = -\frac{\Delta G_3}{zF} \qquad (4)$$

where F is the Faraday constant. The values of E° are given in Table III. According to these thermodynamic data those oxides whose E° is more negative than that of Al_2O_3 will not co-deposit with aluminum, assuming the electrolyte is saturated with the metal oxide. The metal may, however, co-deposit in the aluminum pool at an activity less than 1. However, the magnitude of the cathodic shift in E° is only about 0.2 V for a metal

activity of 0.01 in molten aluminum. Kinetic factors are also not expected to be significant on a liquid metal cathode. Mergault [5-7], Grjotheim et al [8], and Monnier and Grandjean [9] have measured the order of deposition for some oxides using a carbon anode. The resulting series, starting from the least negative potentials is : NiO, V_2O_5, Mo_3O_4, Co_3O_4, Fe_2O_3, WO_3, TiO_2, Nb_2O_5, Cr_2O_3, Ta_2O_5, UO_2, Al_2O_3. The oxides that were more stable than Al_2O_3 were BeO, MgO, CaO, SrO, BaO, and La_2O_3.[3] The order of the former series of oxides is in reasonable agreement with that shown in Table III. The order of the latter series was not obtained as decomposition potentials were higher than that for alumina.

The metal can also dissolve in the aluminum pool through a metallothermic type reaction :

$$MeF_n + \frac{n}{3}Al == \frac{n}{3}AlF_3 + Me \qquad (5)$$
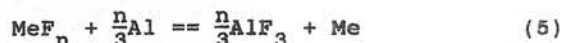
The thermodynamic data for this exchange reaction are given in Table IV.

Tables III and IV indicate that there are a few metal oxides capable of resisting attack by electrolytic and metallothermic reduction into the product aluminum. These are MgO, SrO, La_2O_3, Nd_2O_3, CaO, Ce_2O_3, Sc_2O_3, Y_2O_3, and possibly Li_2O, BaO, UO_2, and BeO.[3] The second criterion indicates that all

Table III. Oxide Decomposition Potentials at 1300 K

OXIDE	$-E_3^\circ$ (V)	OXIDE	$-E_3^\circ$ (V)	OXIDE	$-E_3^\circ$ (V)
PbO_2	0.043	FeO	0.987	CeO_2	2.115
Rh_2O_3	0.054	ZnO	1.052	TiO	2.158
CuO	0.206	Mn_2O_3	1.067	*Al_2O_3	2.173
Cu_2O	0.380	V_2O_5	1.069	Li_2O	2.180
Bi_2O_3	0.409	Na_2O	1.117	BaO	2.202
PbO	0.466	Ga_2O_3	1.146	ZrO_2	2.213
SbO_2	0.597	VO_2	1.302	UO_2	2.234
NiO	0.640	Cr_2O_3	1.363	MgO	2.375
Sb_2O_3	0.647	Nb_2O_5	1.386	SrO	2.397
CdO	0.705	MnO	1.486	BeO	2.440
CoO	0.727	Ta_2O_5	1.529	La_2O_3	2.462
K_2O	0.748	V_2O_3	1.544	Nd_2O_3	2.484
SnO_2	0.813	B_2O_3	1.638	Sm_2O_3	2.505
Fe_2O_3	0.842	VO	1.638	CaO	2.592
GeO_2	0.846	SiO_2	1.757	Ce_2O_3	2.599
WO_3	0.879	TiO_2	1.822	Sc_2O_3	2.621
WO_2	0.911	Ti_2O_3	2.007	Y_2O_3	2.643

361

Table IV. Free Energy of Reaction for Metal - Fluoride Exchange at 1300 K

FLUORIDE	ΔG_5 (kJ)	FLUORIDE	ΔG_5 (kJ)	FLUORIDE	ΔG_5 (kJ)
WF_6	-989	VF_3	-317	KF	3
PbF_4	-976	CdF_2	-306	UF_3	6
VF_5	-785	PbF_2	-299	NaF	13
CoF_3	-657	CoF_2	-283	BeF_2	52
WF	-646	FeF_2	-257	LiF	90
BiF_3	-555	ZnF_2	-257	MgF_2	109
VF_4	-553	CrF_2	-180	NdF_3	167
NbF_5	-481	TiF_4	-165	ScF_3	179
MnF_3	-466	MnF_2	-163	BaF_2	195
CuF_2	-430	SiF_4	-126	CaF_2	211
FeF_3	-422	TiF_2	-78	SrF_2	221
TaF_5	-375	ZrF_4	-46	YF_3	251
CrF_3	-353	UF_4	-42	CeF_3	259
CuF	-340	TiF_3	-42	LaF_3	289
NiF_2	-329				

of these oxides have or will probably have significant solubilities in cryolite. For this reason these oxides have not been of great interest in anode formulations to date. However, the high solubility must be viewed in the light of their resistance against further decomposition. Simply stated, it is not so important that the oxide resist dissolution : it is extremely important, however, that the oxide resist exsolution.

Cerium oxide has been proposed for use as a self forming anode (s.f.a.) material (10). The desirability for the use of such a material becomes apparent from the consideration of the above criteria. The oxide will go into solution with cryolite, but only contaminates the metal pad in low concentrations. Since ΔG_5 for the material is strongly positive it can be easily removed from the metal pad and returned to the cell. Since δ probably equals 1 for this material it has the additional attribute of a solubility that is inversely proportional to oxygen pressure, i.e., it becomes more resistant the harder the cell is driven.

Oxides like Fe_2O_3 have been used in inert anode formulations[2](11), largely due to their low solubility in the electrolyte. Consideration of the other criteria demonstrates the weakness in using solubility as the only criterion for selecting materials. Fe_2O_3 does not satisfy the first criterion, the[2]"crucible reaction"; thus, only if the oxygen evolving on the anode completely removes dissolved aluminum form the melt can Fe_2O_3 be spared from attack by metallothermic reduction. From the standpoint of the second criterion Fe_2O_3 looks attractive; in fact, a relatively low solubility has been measured. Nevertheless, this oxide still does not meet the second criterion because it does dissolve in the electrolyte as do all oxides. Fe_2O_3 does not meet the third criterion because it is decomposed electrolytically, and iron reports to the molten aluminum product. As well, AlF_3 forms in preference to either of the iron fluorides. Thus, the fourth criterion is not met, and the metal can be metallothermically displaced from the melt as well. This also indicates that it would be difficult to remove the iron from the aluminum product through the addition of AlF_3. So while the solubility of Fe_2O_3 in the melt appears to be low, a more complete consideration of the other criteria show that this property is insufficient to make the material acceptable as an anode. It has been suggested (12) that corrosion may be reduced by the addition of Fe_2O_3 to the cell through additions to the feed. While this may slow down the "wear rate" of the anode, the iron will deposit in the aluminum and contaminate the cell product.

In addition to the above issues one must also address problems of adequate electrical conductivity along with a variety of design considerations. However, as a result of having done a materials systems analysis, a number of candidate oxides has been identified for further research.

TESTING OF CANDIDATE FERRITE ANODE MATERIALS

This laboratory has been involved with the measurement of electrical conductivity of anode materials and the testing of these materials in a bench - scale Hall cell. Ferrite materials were chosen for study because of earlier industrial interest in them (13-17). Some Hall cell testing results taken on a single crystal of cobalt ferrite have been previously reported (18). Not reported in that paper are some interesting results obtained from a subsequent SEM examination of the interface layer between the ferrite sample and the electrolyte as shown in Figure 3.

The sample was electrolyzed at 3.0 V, 1 A/cm^2, for about 1 hr in an alumina saturated bath containing 5% CaF_2 at a bath ratio of 1.11 and a temperature of 960°C. Figure 3 shows first a normal SEM micrograph with the cobalt ferrite crystal at the left and the frozen electrolyte at the right. The contrast was reversed for the other micrographs so that the elemental trace would show. The light square at the left side of each micrograph indicates the position on the sample represented in the chemical analysis trace and defines the zero concentration baseline for the profiles. This sample shows a reaction zone of about 8 μm in thickness. The reaction zone for a cobalt ferrite sample of identical composition tested in an electrolyte of the same composition for the same immersion time and electrolyzed only at 2.00 V was 25 to 30 μm thick with similarly shaped profiles. The current density for the sample electrolyzed at 2 V increased from 0.20 to 0.29 A/cm^2 during electrolysis. The profiles indicate that the reaction zone is mostly oxide with a small amount of fluoride. The concentrations of iron and cobalt show a gradual decline towards the outside of the
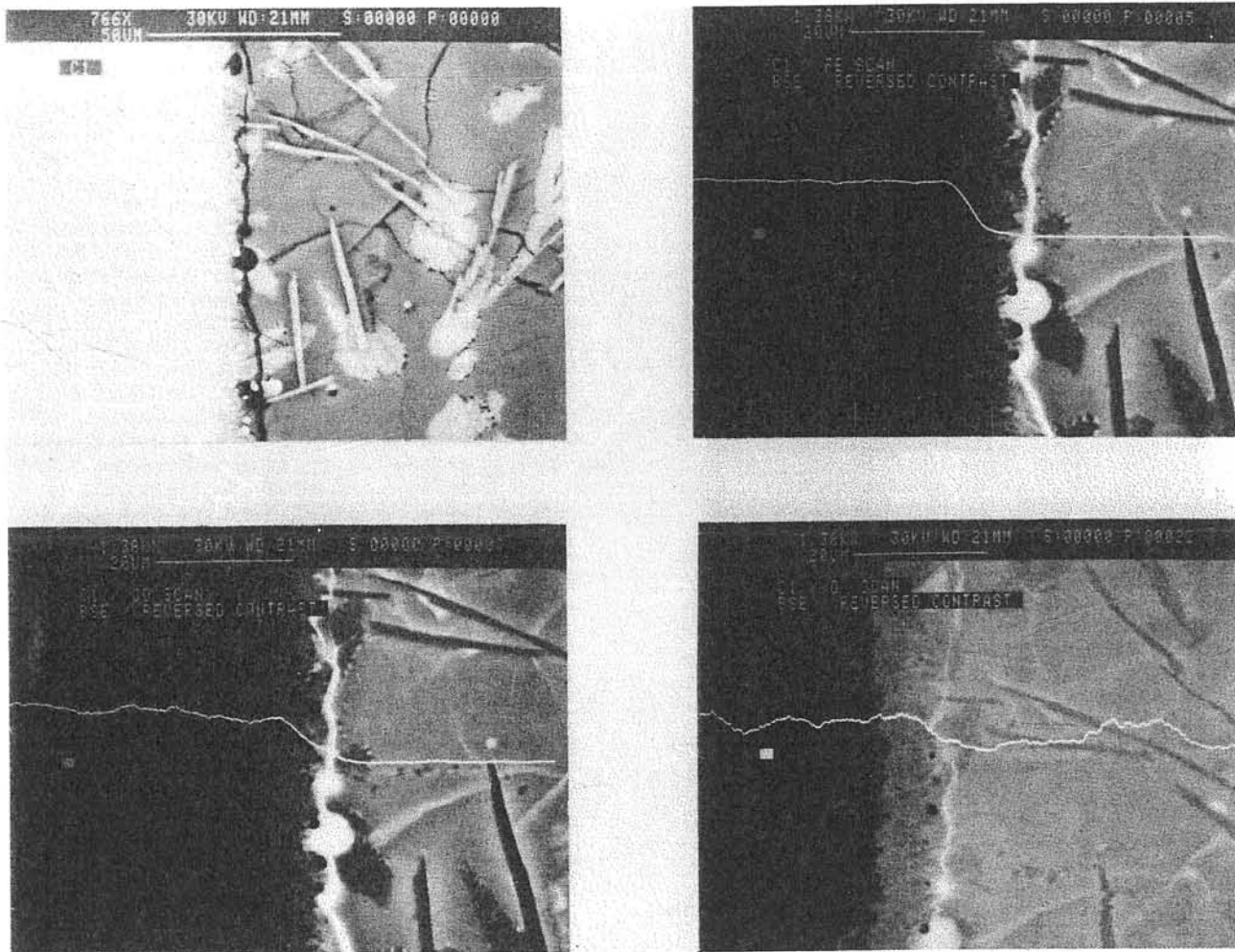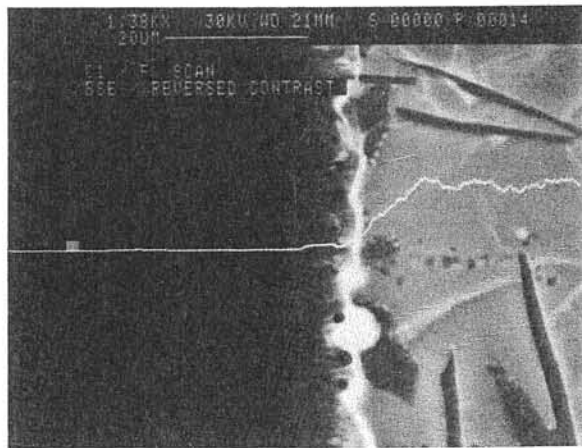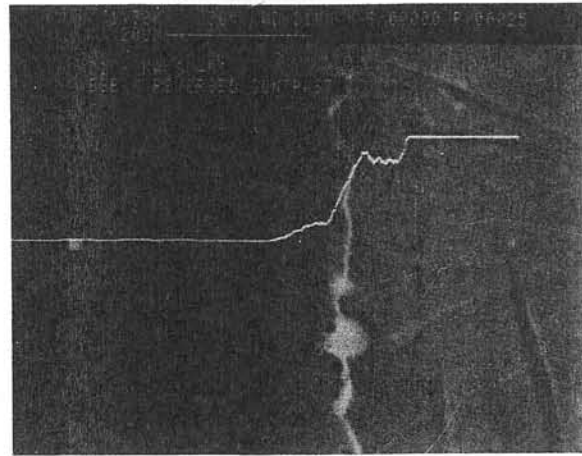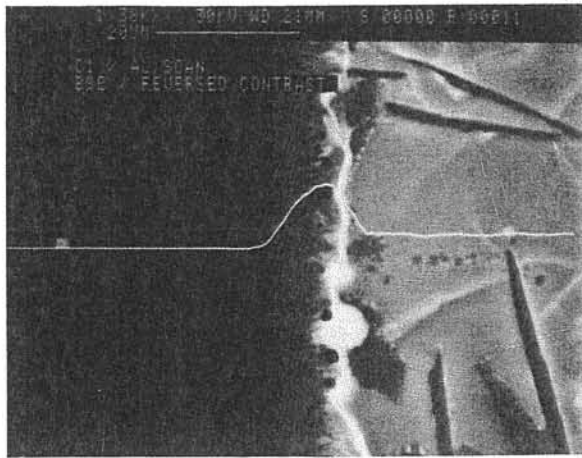

Figure 3. Scanning Electron Micrographs and Elemental Concentration Profiles of the Ferrite - Salt Interface Region for a Cobalt Ferrite Crystal Sample (25 wt% CoO in Fe_2O_3) Electrolyzed at 3.0 V, 1 A/cm^2, for 1 hr, in an Electrolyte of BR = 1.11, Containing 5% CaF_2, 11% Al_2O_3, in Greenland Cryolite, at 960°C.

(Figure 3 cont.)

zone. The most interesting feature is the high concentration of aluminum in this zone. Microprobe analyses indicate that the aluminum concentration is higher than the concentrations of iron and cobalt combined as well as being higher than the aluminum concentration in the salt. This is reasonable in view of the fact that the activity of Al_2O_3 is one in the melt and zero in the bulk of the cobalt ferrite anode. This chemical potential gradient is the driving force for the formation of an alumina rich solid solution. For the zone to grow aluminum must diffuse from the melt through the interface to the ferrite, while cobalt and iron must diffuse from the ferrite to the melt.

The reaction zone keeps the ferrite from coming into direct contact with the electrolyte. Since iron and cobalt must diffuse through the layer the dissolution process predicted in Part 1 will be slowed down. However, the process does not stop,

and any iron and cobalt that go into solution in the electrolyte will certainly co-deposit with aluminum. It may be that the "wear rate" is low enough as a result of this protection. The zone will continue to grow, however, and at longer times may cause an unacceptable increase in the electrical resistance of the anode.

ACKNOWLEDGEMENTS

REFERENCES

1) K. Billehaug and H. A. Øye, "Inert Anodes for Aluminum Electrolysis in Hall-Héroult Cells," Aluminum (Düsseldorf) 57(2)(1980), 146-150; 57(3)(1980), 228-231.

2) I. Barin and O. Knacke, Thermochemical Properties of Inorganic Substances (Berlin: Springer - Verlag, 1973).

3) I. Barin, O. Knacke and O. Kubaschevski, Thermochemical Properties of Inorganic Substances Supplement, (Berlin: Springer - Verlag, 1977).

4) K. Grjotheim, C. Krohn, M. Malinovský, K. Matiasovský, and J. Thonstad, Aluminum Electrolysis, Fundamentals of the Hall - Héroult Process, 2nd edition, (Düsseldorf: Aluminum - Verlag, 1982)

5) P. Mergault, "Tension de décomposition de quelques solutions d'oxydes dans la cryolithe fondue," C. R. Acad. Sci.,

Paris 240(1955), 864.

6) P. Mergault, "**Tension de décomposition de solutions d'oxydes dans la cryolithe fondue**," _C. R. Acad. Sci., Paris_ 240(1955), 1568.

7) P. Mergault, "**Tension de décomposition des solutions cryolithiques d'oxydes de titane, vanadium, niobium, tantale, uranium, molybdène et tungstène à 1020°C**," _C. R. Acad. Sci., Paris,_ 240(1955), 1755.

8) K. Grjotheim, "Série électrochimique des métaux dans les fluorures fondus," _Revue de l'aluminum,_ 31(1954), 129.

9) R. Monnier and P. Grandjean, " Recherches sur l'obtention, la séparation et la purification de tantale et du niobium, notamment par voie electrochimique. II Etude d'une methode de determination des tensions effectives d'électrolyse et des tensions pratiques de décomposition; application de cette methode à des solutions cryolithiques d'oxydes," _Helv. Chim. Acta,_ 43(1960), 2163.

10) J.-J. Duruz, J.-P. Derivaz, P.-E. Debely, I. L. Adorian, (Eltech Systems Corp.), "Molten Salt Electrowinning Method, Anode and Manufacture Thereof," Int. Pat. App. No. WO 84/02724 (1984).

11) S. P. Ray and R. A. Rapp, (Alcoa), "Composition Suitable for Inert Electrode," U.S. Pat. No. 4,455,211 (1984).

12) R. Keller, "Method to Improve the Performance of Non-consumable Anodes in the Electrolysis of Metal," U.S. Pat. No. 4,504,369 (1984).

13) F. W. Baker and R. L. Rolf, "Hall Cell Operation with Inert Anodes," _Light Metals 1986,_ R. E. Miller, editor (Warrendale, PA: TMS-AIME, 1986), 275-286.

14) S. P. Ray, "Inert Anodes for Hall Cells," ibid., 287-298.

15) D. H. DeYoung, "Solubilities of Oxides for Inert Anodes in Cryolite-Based Melts," ibid., 299-308.

16) G. P. Tarcy, "Corrosion and Passivation of Cermet Inert Anodes in Cryolite-Type Electrolytes," ibid., 309-320.

17) J. D. Weyand, "Manufacturing Processes Used for the Production of Inert Anodes," ibid., 321-341.

18) A. D. McLeod, J. S. Haggerty and D. R. Sadoway, "Inert Anode Materials for Hall Cells," ibid., 269-273.