

Introduction

Over the past few years the combined effects of recession, escalating power costs, and low metal prices have pushed the U.S. aluminum industry into a precarious position, unable to compete with foreign imports (1). In order to retain a competitive position and maintain a U.S. aluminum business onshore, new energy efficient and less labor intensive processes must be developed for producing primary metal.

Carbothermic direct reduction has been proposed as an alternative to the present day electrolytic reduction cell (2,3). However, this technology is in its infancy and a considerable number of technological hurdles must be overcome (4,5).

Substantial advances have already been made in terms of optimizing cell design in modern prebake smelters. Cell simulation computer modeling (6) has been of immense importance in guiding the systematic redesign of the current-carrying busbar arrangement and hence diminishing magnetic interaction with the metal pad. A number of companies now have large prebake cells available with energy efficiencies in the range 5.5-6.5 kWh/lb (7,8,9,10).

However, the improvements possible with the present basic design of carbon cathode cell are limited by the need to maintain a molten aluminum pool on the cathode surface. Aluminum does not wet carbon, which means that a certain minimum height of molten metal must always be present to ensure good physical and electrical contact with the cell bottom. The head of metal must also be sufficient to prevent bath material from interposing between the metal pad and carbon lining. Consequently, between the anode and the carbon cell bottom there must always be a significant thickness of metal, which is subject to electromagnetic stirring under the influence of the high operating currents. This stirring displaces the surface of the liquid metal cathode, and the instability of the bath-metal interface can cause metal to become entrained in the bath. The anode-cathode distance can therefore only be narrowed by a limited amount before back reaction, shorting, and loss of current efficiency become a problem.

Solid Cathode Technology

The potential advantages of dimensionally-stable, aluminum-wettable "solid cathodes" for aluminum smelting cells are well documented (11,12). In principle, such cathodes should permit a revolutionary redesign of the conventional Hall-Heroult cell since the molten aluminum can be made to drain away from the cathode surface. In this way, the electrolytically-produced molten metal pool can be removed from the anode-cathode gap to a location where electromagnetic interaction is less and does not result in a loss of current efficiency. The distance between the anode and the solid cathode can then be reduced substantially, since the magnetic forces on a thin film of electrodeposited aluminum are negligible compared to those on a deep pad.

Various means have been proposed for separating the deposited metal from the anode-cathode gap. Designs have been tested using refractory hard material (RHM) cathode bars (13,14) in the bath layer causing the product aluminum to fall into a collection pool well below the anode. Various shaped RHM protrusions (cylinders, pipes, tables, grids, etc.) extending above the metal pad have been tried (15,16). Sloping cathodes which drain downhill to a metal reservoir were among the first to receive attention

USE OF TiB₂ CATHODE MATERIAL:

DEMONSTRATED ENERGY CONSERVATION IN VSS CELLS

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A new, durable, carbon/TiB₂ material has been tested and proven in a plant trial at The Martin Marietta Aluminum, Northwest Operations, West Unit (The Dalles). Ongoing metal analysis for titanium and boron continues to show uniform and slow coating wear, dominated by the rate of TiB₂ dissolution in molten aluminum. Significant energy efficiency benefits were also noted for the TiB₂-coated cells compared to the rest of the plant, but in the absence of a valid group of control cells, it was not possible to draw firm conclusions. Accordingly, a fully controlled and monitored 12-cell experiment was set up at the Martin Marietta Aluminum, Northwest Operations, East Unit (Goldendale) to investigate the improved energy efficiency. After 18 months in service, the test cells have shown consistent benefits relative to the control cells and the plant. The observed advantages are largely attributed to improved cathode current distribution and a cleaner cathode surface, which result in a quieter metal pad, thus allowing the cell to be operated at lower set voltage.

(14,17) and were recently subject to detailed investigation in a large DOE-sponsored project (18). Recent literature reports (19,20) describe the use of RHM chunks or rubble on the cathode lining, which permits electrolysis on the uppermost layer of the RHM pile while damping the movement of the metal pad situated lower in the pile.

There has been only very limited experimental success with any of these approaches. The fragility and poor thermal shock resistance of large RHM parts extending into the electrolyte resulted in excessive breakage with extremely high replacement cost. The methods employing flat anodes and horizontal cathode configurations have typically not achieved the predicted energy savings because of high apparent bath resistance, and low current efficiency when the ACD is reduced by any significant amount. Rubble cathodes and complex RHM projections from the cathode floor have been plagued by difficulties in avoiding and remedying the accumulations of sludge and undissolved alumina on the cell bottom. Techniques such as sloped cathodes, involving RHM surfaces on a conventional carbon substrate, have failed because of intergranular corrosion of the material and attachment difficulties.

Carbon/TiB₂ Composite Materials

One of the cornerstone issues in developing a low energy cell (LEC) has been the need for a low cost, durable RHM material. In a paper given at this conference last year we reported on the results of a successful materials test at the Martin Marietta Aluminum, Northwest Operations, West Unit (The Dalles, OR) (21,22). A carbon/TiB₂ material developed at Martin Marietta Laboratories (23) was installed as a spread coating on the cathodes of six conventional VSS aluminum cells. Ongoing metal analysis and cathode core samples, taken during a scheduled shutdown period, showed that the TiB₂ material was extremely durable and resistant to the aluminum cell environment. A more recent core sample taken from one of these coated cells that had been in operation for 2 years still showed a substantial thickness of carbon/TiB₂ material in the area prepared for coring.

There have been sporadic references in the patent literature to other forms of carbon/TiB₂ composite materials for aluminum cell cathodes. One of the earliest types, tested by Lewis and Hildebrandt (17), was based on a typical cathode ramming paste of highly calcined coke and pitch. TiB₂ powder or TiB₂ precursor materials were added to the pitch prior to blending with the aggregate, and the paste was then rammed onto the cell floor. However, when TiB₂ is formed by in-situ reaction during bake, the resultant body has been found to be soft and friable (24) and even the blend of TiB₂ powder and pitch shows poor durability under cell operating conditions (25). More recent work by Das et al. (26) has focussed on the use of a wholly graphitic matrix in which the TiB₂ is imbedded. However, tested wear-rates reported for this material were extremely high and preclude the possibility of practical implementation. Similar work by Joo' et al. (24) entailed graphitization of coke/pitch/TiB₂ blends or graphitization of the carbon materials concurrent with in-situ formation of TiB₂. Again, the resulting carbon matrix is soft and readily forms aluminum carbide under cell operating conditions.

The material invented at Martin Marietta Laboratories has circumvented the shortcomings of the prior art by employing a particular specification of TiB₂ powder and a unique carbon matrix. The carbon matrix is chosen for granulometry compatible with the required cure and bake procedures, while the types of carbon solids and binder phase are blended in such a way as to provide the most chemically and physically rugged mix of hard and soft carbons (27).

In addition to the unique durability of this material, the performance of the six TiB₂-coated test cells was far better than that of the plant. Comments from the cell operators indicated that the energy efficiency benefits might derive from the consistently cleaner cathode surface and absence of hard "muck." This was confirmed with some preliminary cathode collector-bar current distributions which were much more uniform in the test cells than in the rest of the plant. The experiment at The Dalles was not considered fully conclusive, however, because of the differences in average age and cathode block type between the test group and the rest of the plant.

Another plant trial was therefore set up at the Martin Marietta Aluminum, Northwest Operations, East Unit (Goldendale, WA). Because of a recent plant expansion, completed in January of 1983, 12 adjacent new cells could be coated and compared with 12 identical control cells in the same section of the room. This set-up had the advantage of comparing directly between cells of the same design, the same age, and the same operating personnel. The project was sponsored as a cost-sharing venture with the Bonneville Power Administration as a potential energy conservation resource under contract DE-AC-79-83BP13770.

The Plant Trial at Martin Marietta Aluminum, Northwest Operations, East Unit

In the East Unit plant trial one whole section at the east end of D room was devoted to the test, with the coated cells on one side and the control cells on the other side of the service aisle (Figure 1). Every attempt was made to ensure that there was no bias toward either group of cells. Each group contained newly constructed cells with the same mix of block types, and all of the cells in the section were of the same design, insulation, and anode construction. Of particular importance to the experiment was the fact that all of the test and control cells were started within the same 3-month period, and since that time both groups have always been operated under the direction of the same foreman and general foreman.

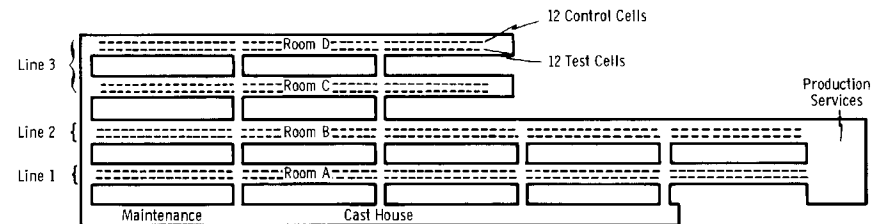


Figure 1
Schematic of the East Unit plant showing the location of the experimental cells

Table I. Frequency of Data Collection

Measured Parameter	Quantitative Data		Method of Measurement*
	Routine Data Collected for Project (Number per month)	Additional Data Taken By Project Technicians (Number per month)	
Cell Voltage	Daily	-	C
Set Point Voltage	Daily	-	M
Anode Effect Frequency	Daily	-	C
Anode Effect Voltage	Daily	-	C
Line Current	Daily	-	C
Pot Noise	Daily	-	C
Back E.M.F.	Daily	-	C
Metal Tap	15-16	-	M
Metal Pad Height	4-5	-	M
Bath Pad Height	8-10	-	M
Bath Temperature	4	-	M
Bath Ratio	4	-	M
Metal Purity	6-8	-	M
Metal Inventory	-	1	M
Cathode Voltage Drop	1	1	M
Anode Voltage Drop	1	1	M
Current Efficiency	Daily	-	C
Specific Energy Consumption	Daily	-	C
Cathode Current Distribution	-	2	M
Anode Current Distribution	-	2	M
Cathode Shell Temperature	-	4	M
Anode Leg	-	4	M
Skirt Gap	-	4	M
ACD	-	4	M
Ti and B analysis	-	4-5	M
	Qualitative Data		
Anode Problems	-	Daily	M
Muck Problems	-	Daily	M
Muck and Ledge Surveys	-	7-10	M
Operation Problems	-	Daily	M

* C represents a computer measurement, M is manual

The additional BPA funding made it possible to set up an extensive monitoring program between September 30, 1983 and September 30, 1984. The parameters included in this program are listed in Table I. Two full-time data technicians, analytical services, and a project manager were dedicated to the experiment, which permitted a comprehensive analysis of the difference between test and control groups. Extraneous factors such as anode upsets were to be tracked and used to explain anomalous data on a cell-by-cell basis, and the secondary performance indicators in both groups were compared to ensure that both groups were being operated in exactly the same way.

The coating procedure used in the West Unit plant trial was modified somewhat because the East Unit cells had already been lined and rammed, so it was not possible to coat, cure, and bake the individual cathode blocks. Instead, the coating was applied directly to the cell floor in one operation, then cured and baked in-situ.

Improved coating formulations developed from the results of the ongoing West Unit test permitted individual adjustments to be made from cell to cell, making slight variations in the type and amount of the constituents. A parametric analysis was then used to determine which, if any, of the formulation modifications had an effect on the coating performance and/or cell performance. Among the formulation parameters varied were TiB₂ type, carbon fiber type, and the amount of binder phase. Other variables within the test group included cathode pretreatment (prebaking), start-up procedure, and cathode block type. Accordingly, the study could not be used to generate definitive information on each variable but was useful in indicating the relative importance of each.

Comparison Between the East Unit and West Unit Plant Trials

Perhaps the most important distinction between the two plant trials was the difference in comparison group. At the West Unit the TiB₂-coated cells were compared in performance with the whole plant, so that the differences in cell age, cathode block type, operator skill, etc. were not taken into account. The East Unit test was excellently controlled since 12 control cells in the same locality, and of equal age, block types, cell design, and operators were available. In addition, the data collection at the East Unit was much more thorough and comprehensive which permitted the detection of individual cell problems and correlation of experimental variables with performance, and ensured rigorously equitable treatment of both groups.

The remaining differences between the two plant trials relate more to the physical set-up and performance of the experiments. At the West Unit only Sumitomo Kiowa (SK) blocks were coated, whereas at the East Unit there were three different types of cathode block in each group: SK, Savoie, and G.R. Stein. Because of the block location and increased area coverage at the East Unit, procedural modifications were also necessary, and novel application techniques were developed. Coating single SK blocks external to the cell had not required any major surface preparation, whereas it was necessary to roughen the block surface heavily for in-situ coating of the entire cathode surface. However, there were a number of benefits derived from working with a cathode that had already been lined. With practice, the actual spreading time for a whole cathode was reduced to 2-3 hours, compared to single block coating, which typically required one week per cathode because of space limitations in the cure ovens. Additionally, the

cure and bake could be performed in one operation, since the same convection furnace was used for both. This eliminated all the block handling, and other space-, equipment-, and labor-intensive processes.

Coating the whole cathode surface in one operation also provided an opportunity to experiment with the area of coverage. In the plant trial at the West Unit the entire surface of each block was coated, but the ram slots between them were left uncovered. In the full cathode experiments at the East Unit, only the inner half of all the perimeter blocks was coated in order to limit the extension of the frozen side ledge to the boundary of the coating. The adhesion of bath/alumina-type materials to the TiB_2 coating is very poor compared to the adhesion to carbon. Thus, the frozen side ledge is constrained to some degree to remain only on the uncoated portion of the cathode (28). The in-situ process also permitted experiments to be run with coating applied over some or all of the ram joints. This is important if the coating is behaving as a protective barrier and prolonging the life of the cell, because the ram slots are traditionally regarded as the areas most prone to bath and/or metal penetration and consequent failure.

Finally, at the East Unit, the use of new cells which had never been in operation, rather than old, relined cathode shells, allowed two new procedures to be tested. First, it was possible to test the feasibility of starting up a coated cathode concurrent with anode bake-in using a standard "candle-start" procedure. The effect this had on coating wear could then be compared with cells which had been "coke-started" with a prebaked anode. Second, some of the test cathodes had been prebaked before the coating was applied. These were compared with standard rammed cathodes.

The Twelve-Cell Test

Application, Cure, and Bake

Preliminary experiments at Martin Marietta Laboratories had shown that the cured bond between the TiB_2 coating and the cathode block substrate was very weak in the vicinity of the cathode ram slot. Accordingly, a technique was developed which increased the block-to-coating bond strength and allowed the pitch volatiles to vent from the top surface of the ram joint. Initially, the block surface was roughened heavily with a scabber to increase the keying of the coating to the carbon. Inverted "U" channel aluminum extrusions were then nailed in place over the ram joints to permit volatile release and to serve as depth guides for spreading. In some cases, channels were installed over all of the ram slots; in others, they were only placed over the longitudinal joints. Because no problems with volatile release were experienced in either case, experiments were run on two cells where the channels were removed after cure, and the exposed ram was then fully coated as well. The performance achieved with cells carrying a uniform monolithic coating across the whole cathode area could then be compared with cells in which the aluminum wetting properties were interrupted by discontinuities at the ram slots.

Because of low ambient temperatures (the coating was installed in the early winter of 1982), the cathode lining and the coating mix were preheated to facilitate spreading. To do this, the cathode was covered with tarpaulins and heated overnight with propane-fired industrial space heaters and the mix was prepared in a 40-gallon double planetary mixer equipped with a hot-water jacket.

The green mix was applied to the roughened cathode surface by trowel and then screeded to the height of the depth frames with a steel bar. The curing operation was started on the same day using a large convection furnace designed to rest on the deck plate of the cathode shell (Figure 2). The furnace was controlled from thermocouples in the gas exiting the exhaust nozzles, and was programmed to follow the requisite cure cycle by correlating this temperature with the temperature of various thermocouples imbedded in the coating. Following cure, the coating was carefully inspected for defects such as cracks and blisters, and any damaged areas were repaired by applying fresh material while the cathode was still warm. During the next heat cycle this material cured simultaneously with baking. The patching process in this instance was considerably simpler than for damaged coatings on single blocks, since it was not necessary to repeat the cure cycle.

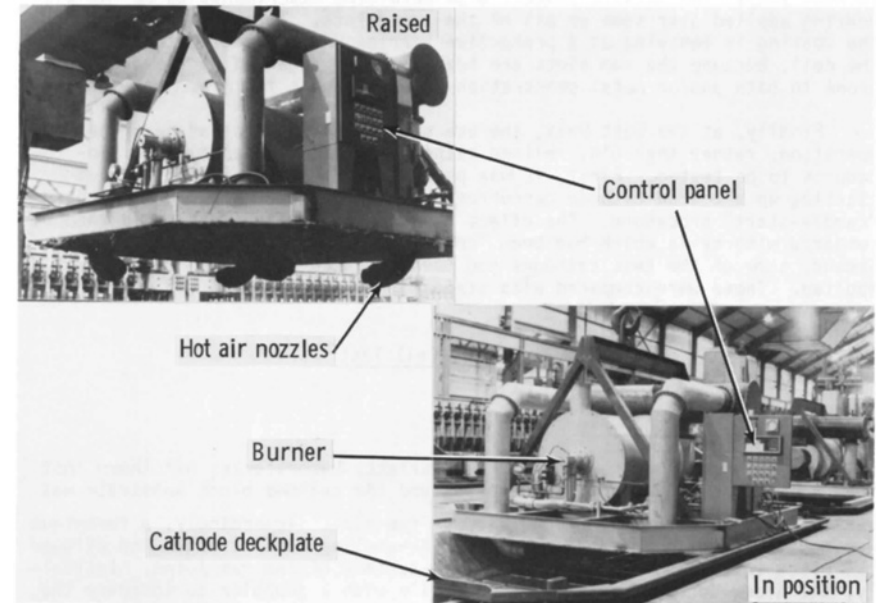


Figure 2
Cathode coating cure and bake furnace

Baking was accomplished with the same furnace; however, early experiments had shown that the sidewalls of the cell were severely oxidized in the 400-600°C temperature range. Since the furnace could not be operated under fully reducing conditions, oxidation protection had to be provided to the TiB_2 coating and the cell sidewalls. Covering the cured coating with calcined coke and protecting the sidewalls with fireproof glass fiber matting, steel sheets, and insulating brick proved very satisfactory, even during protracted bake cycles when most of the coke was consumed. The ultimate bake temperature was between 500 - 650°C and varied from cell to cell since furnace modifications were being tested. One coating was not baked at all, to test whether conventional cell start-up procedures could be used on the material in the cured state.

Cell Operations and Monitoring

All 12 of the control cells were started up and baked concurrent with preparation of the Soderberg anode using a candle-start procedure. Some of the test cells were started in the same way; the remainder were baked-in with a coke start using anodes that had been baked previously in service. Typically, during the early start-up stages the voltage requirement was significantly higher for the coated cells than for the uncoated control cells. After the first few hours, however, the coating had carbonized and the bake-in proceeded at near normal voltage levels.

Cell cut-in was standard, and the operators were given no special instructions on how to run the coated cells. Accordingly, the set voltage of the cell was determined by the normal industry-accepted criteria, such as anode effect intensity, bath action, etc. No attempt, deliberate or otherwise, was made to lower the test cell voltages below that dictated by usual plant practice.

An identical set of data was collected for the test and control groups (Table I). Many of the parameters were routinely monitored by the plant, and only the frequency of measurement was increased for the experimental section. However, because there were full-time technicians dedicated to the project, different types of measurements were possible, including regular copper testing for metal inventory, anode and cathode current distributions, and ledge/muck surveys. This bank of information permitted a comprehensive analysis of the source of benefits in the coated test cells.

Overall Performance Results

Test cell cut-in was completed during the first three months of 1983 so that meaningful data was only available from the second quarter onwards. Current efficiency and energy efficiency values were averaged for both groups on a quarterly basis, to smooth out the month-to-month fluctuations typical of VSS cells. These results have been plotted as current efficiency and energy efficiency differential histograms for the last 3 quarters of 1983 and the first 2 quarters of 1984 (Figures 3 and 4, respectively). Except for the third quarter of 1983, there has been a consistent test cell benefit amounting to approximately 0.15-0.2 kWh/lb and about 1.5% current efficiency. The historical record for the six test cells at the Northwest Operations, West Unit is very comparable (Figures 5 and 6), despite the fact that these cells were compared directly against the plant average instead of a control group.

Very little weight can be attached to the unfavorable comparison between the test and control cells at the East Unit during the third quarter of 1983. In the late summer of 1983 there was a substantial plant-wide upset caused by off-specification shipments of alumina ore and coke raw material for the anode. The problems did not impact all sections of the plant to the same extent, and there was no relation between the performance decline and cathode condition.

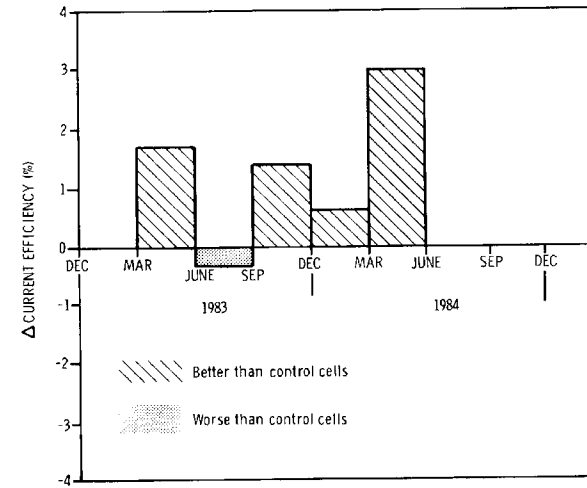


Figure 3
Quarterly differentials between test and control cell current efficiency (East Unit)

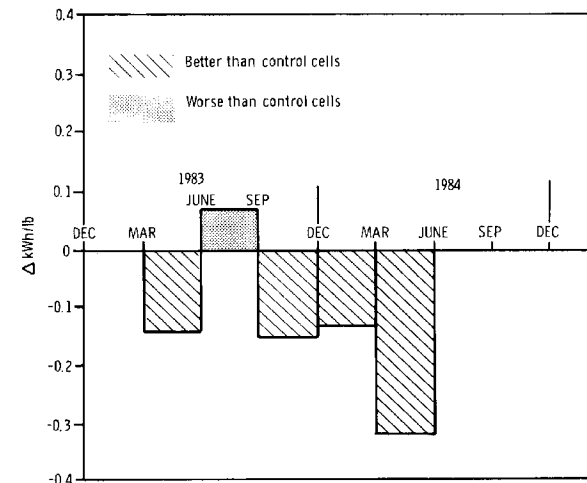


Figure 4
Quarterly differentials between test and control cell specific energy consumption (East Unit)

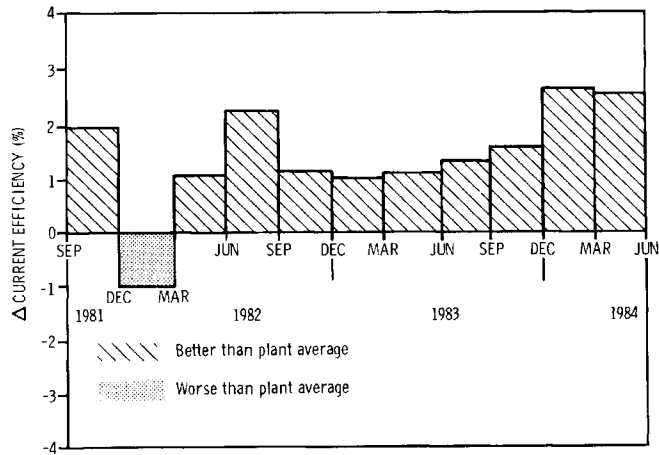


Figure 5

Quarterly current efficiency differentials between test cells and plant (West Unit)

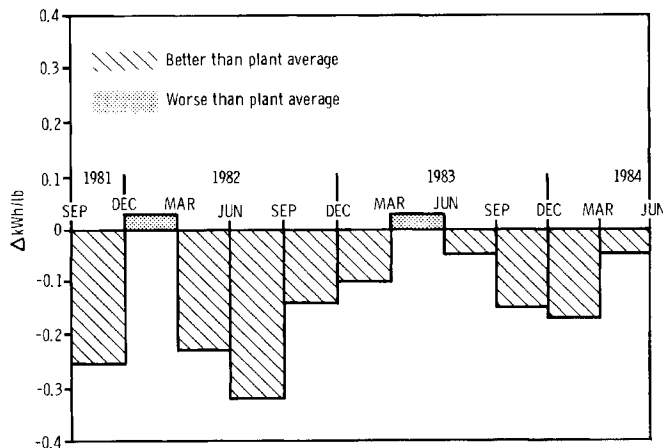


Figure 6

Quarterly specific energy consumption differentials between test cells and plant (West Unit)

In addition to the improvement in energy efficiency, the test cells showed a marked benefit in uniformity of cathode collector bar current distribution. In Figure 7, the difference in collector bar variation coefficient between test and control groups has been plotted as a percentage of the control cell variation coefficient. One of the test cells was omitted from this analysis because there was a tap-out through the sidewall in the first few weeks after cut-in, which electrically isolated one half of a collector bar.

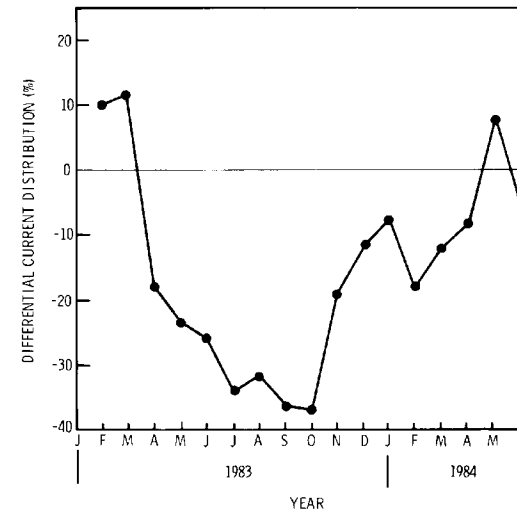


Figure 7

Differential between test and control cell cathode current distribution expressed as a percentage of control

The improvement in collector bar current distribution favorably affects the magnetic and thermal balance of the cell. Accordingly, the perturbations of the bath-metal interface are decreased, and the gap between the anode and the metal pad can be narrowed without loss of current efficiency from shorting and metal fog-anode gas reactions. Obviously the heat input to the cell is decreased because the voltage drop across the bath is lower. However, a cooling effect is not seen, because the "natural insulation" of the cell (the frozen side ledge) compensates for the lower input by thickening.

Early measurements made in the six test cells at the West Unit had indicated significant savings in cathode voltage drop compared to the plant average. In the more closely controlled test at the East Unit, no consistent differences were observed between the test and control groups in this regard. In fact, the magnitude of the cathode voltage drop was dominated by the type of cathode block and various external factors that affected the cleanliness and ledge extension onto the cathode surface.

Some attempts were made to account for the relative difference in energy efficiency between test and control groups by assigning some of the

benefit to increased current efficiency and the remainder to lower operating voltage. Although the distribution between current efficiency and voltage fluctuated, it typically divided about 50:50. This indicates that it was possible to operate the test cells with a narrower ACD (lower set voltage) and still avoid loss in current efficiency through back-reaction or shorting. Again this points to improved metal pad stability.

One of the most compelling pieces of evidence that there were real distinctions between the TiB₂-coated test cells and the control group, was the strong endorsement by operating personnel. First-hand observation of the TiB₂ cathodes made it clear that they were easier to run than conventional carbon cathodes. The cell bottoms were consistently less mucky than the cells in the control group, and they recovered from upset much more rapidly. Two features in particular drew comment from the cell operators: first, the very clean cathode surface and total absence of hard muck accumulations; second, the lower set voltage that was possible while still maintaining good bath action, high anode-effect-intensity, and high current efficiency.

Secondary performance factors were also monitored throughout the life of the test cells. These were compared between groups to establish trends and to detect any bias in treatment of either group. In Figure 8, some of the monthly differentials between corresponding parameters in the two groups have been plotted as a percentage of the value of that parameter in the group that is numerically lower. Thus, for example, a point plotted as 6% positive indicates that the test cell average was 6% higher than the control cell average. A point 6% negative shows that the control cell average was 6% higher than the test cell average. Overall, the analysis shows no particular trend since neither group was consistently higher on any of these ratings. This is strong evidence that, although the test cells were producing more metal at lower specific energy consumption than the control group, the thermal balance of the cell was able to adjust to accommodate the reduced heat input.

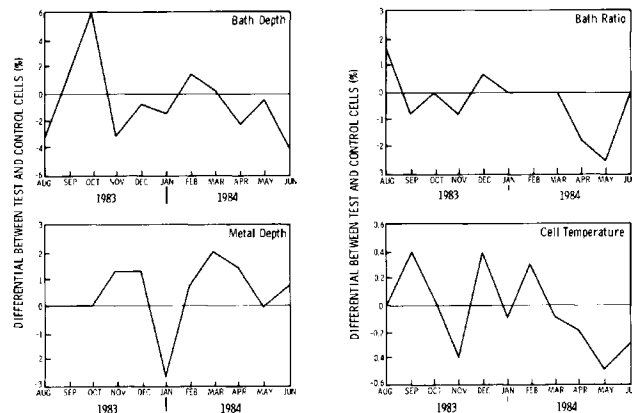


Figure 8

Comparison of some secondary performance parameters expressed as a percentage differential between test and control groups

Coating Performance and Wear Mechanism

Titanium and boron concentrations in the metal pad were routinely measured five times per month on each test and control cell. The accuracy of the measurement was increased from two to four decimal places of wt% by using high precision standards on the spark analysis spectrophotometer. The assay numbers were then treated in two different ways.

To establish how fast the TiB₂ coating was being lost to the aluminum metal pad, we had to calculate a base level of titanium for a conventional cell that receives titanium only from the alumina and the anode carbon. On any particular day, this background concentration was calculated from the average titanium level in the uncoated control cells. For any test cell, the amount of TiB₂ lost from the coating in a given metal tap was calculated as:

$$TiB_2(\text{loss}) = \frac{Ti(1) - Ti(ca)}{100} \times \text{Tap wt.} \times \frac{69.52}{47.90} \quad (1)$$

where TiB₂(loss) is the weight of TiB₂ (in lb) lost to the tapped metal

Ti(1) is the Ti concentration (in wt%) in test cell 1

Ti(ca) is the average Ti concentration (in wt%) in the control cells

Tap wt. is the weight of metal tapped from the cell (in lb).

Only the titanium analysis is considered in this calculation, since boron is not retained stoichiometrically in the metal pad, due to its volatility.

The other calculation used in analyzing the data entailed a comparison between the total measured titanium and boron concentrations in the metal pad and the total amount that can theoretically dissolve at equilibrium at that temperature. To perform this analysis, we assume that the total titanium assay comprises both dissolved and undissolved (or precipitated) titanium. The boron assay is similarly divided:

$$i.e., Ti(t) = Ti(d) + Ti(p) \quad (2)$$

$$B(t) = B(d) + B(p) \quad (3)$$

where Ti(t) and B(t) are the measured total concentrations (in wt%)

Ti(d) and B(d) are the concentrations (in wt%) dissolved at equilibrium

Ti(p) and B(p) are the concentrations (in wt%) remaining undissolved.

Assuming stoichiometric precipitation only as TiB₂, the relation in wt% between Ti(p) and B(p) becomes:

$$Ti(p) = \frac{1}{2} \times \frac{47.90}{10.81} \times B(p) \quad (4)$$

$$Ti(p) = 2.22 B(p). \quad (5)$$

And from the published solubility data, (29) the amount of Ti(d) and B(d) in solution in the metal are given by:

$$Ti(d) B(d)^2 = K_{sp} \quad (6)$$

where K_{sp} is the solubility product (in wt%), which varies with temperature according to:

$$\log K_{sp} = 5.22 - \frac{1.62 \times 10^4}{T(^{\circ}K)} \quad (7)$$

From these relations it is possible to solve for Ti(p) and B(p), which theoretically account for the TiB_2 that is present in the metal pad in particulate or undissolved form.

The plots in Figure 9 show how the different parameters derived above vary with time for a typical test cell. For reference, a temperature profile for the period is given in Figure 9(a). Figure 9(b) shows the variation in total measured titanium concentration with time during 1983. Figure 9(c) is a plot of the calculated undissolved TiB_2 , corresponding to the total titanium analyses in Figure 9(b) and temperature in Figure 9(a). In this example, it can be seen that the TiB_2 is always running over saturation and the average concentration of "particulate TiB_2 " is approximately 20 ppm. Figure 9(d) is a plot of the relative titanium concentration, representing the titanium concentration in the metal pad that can be assigned uniquely to wear of the cathode coating material. This excess concentration is typically 40 ppm. Finally, in Figure 9(e), the excess TiB_2 concentration has been multiplied by the tap metal weight to yield the weight of TiB_2 lost in each metal tap; it amounts to approximately 0.2 lb/tap.

Figure 10 shows the cumulative loss of TiB_2 with time plotted for two cells with different specifications of TiB_2 material in the cathode coating. Evidence accumulated over all 12 test cells has shown that the dramatic difference in loss rate may be ascribed unambiguously to the difference in TiB_2 specifications.

The trends in cumulative TiB_2 loss, such as those shown in Figure 10, can be used to project the coating service-life. This has been done by looking at the average TiB_2 loss-rate during the most recent few months and then calculating how much longer the remaining weight of TiB_2 in the coating will last, if the loss rate remains constant at this level. Extrapolations made in this way every quarter have consistently predicted a coating life of approximately 5 years for type A TiB_2 and 7 years for type B TiB_2 . Since the coating life is directly proportional to the amount of TiB_2 originally present, it can be increased simply by increasing the thickness of the original coating layer.

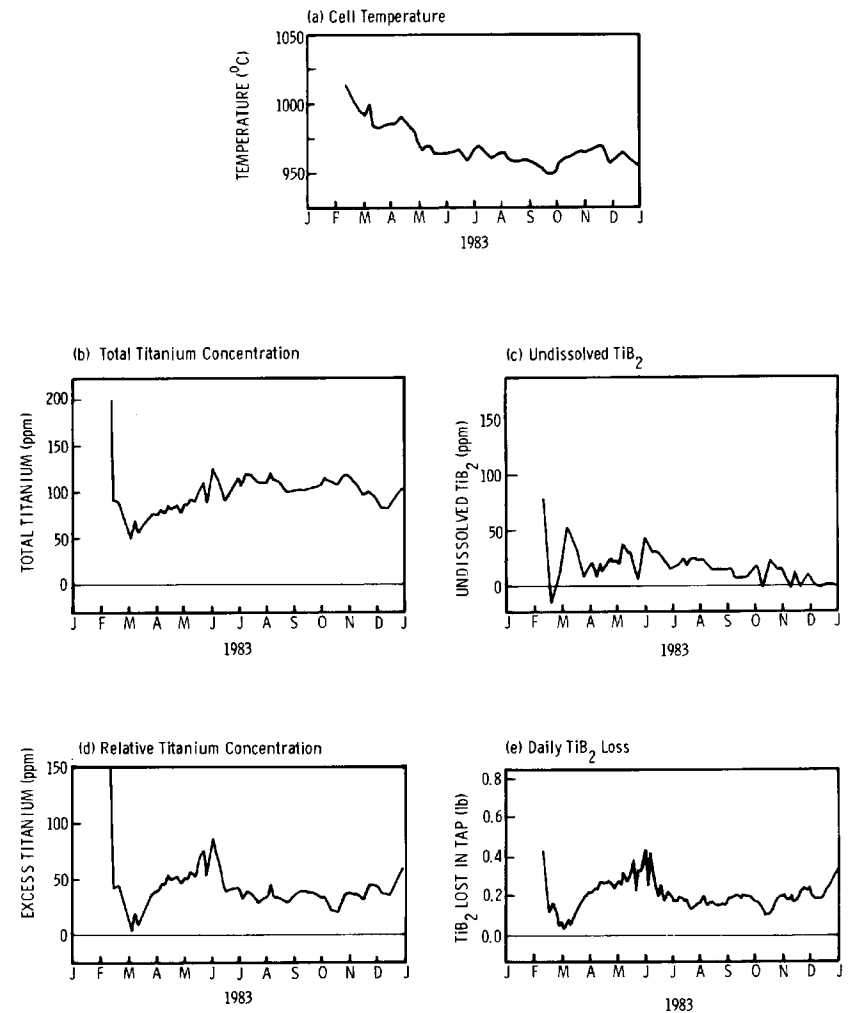


Figure 9
 TiB_2 loss analysis for a typical cell during 1983

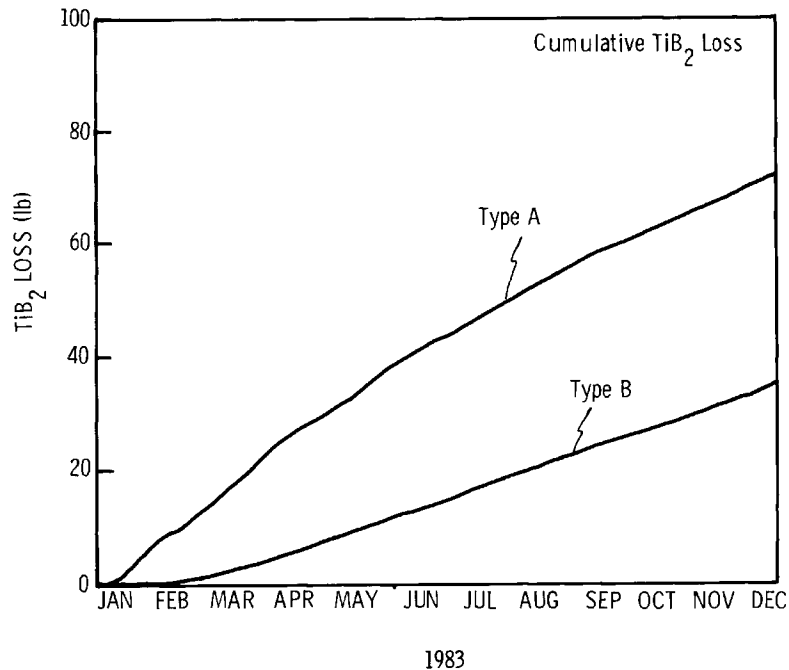


Figure 10

Total accumulated TiB₂ loss due to coating wear for two TiB₂ specifications

The fact that titanium and boron are found in the metal pad at concentrations that are consistently over the solubility limit is somewhat anomalous, because intensive scanning electron microscope (SEM) studies of cut sections of metal taken from the test cells revealed no particulate TiB₂, even in the close vicinity of the coating. Four possible explanations can be advanced. The particles of TiB₂ may be so small as to preclude finding them with any certainty on SEM scans of cut sections. The published solubility product data may be inaccurate. The instantaneous bath temperature measurements may differ from the average metal pad temperature or may not be representative of the true time-averaged temperature. And, finally, there is a possibility that dissolved elements, other than titanium and boron, may precipitate independently with the boron and titanium. Each of these hypotheses is considered in order below.

In SEM pictures at a magnification of 30,000, it should have been quite possible to resolve particles down to 0.1 μm but anything less is probably below the critical nucleus size.

The solubility product data (29) used in these calculations represents the best fit to the experimental data of five separate workers. The authors are also aware of recent, independent confirmation of the same data.

Calculations were made to ascertain whether the relatively high Ti and B analyses could, in fact, have been solubility limited, but at a higher temperature. In Figure 11, temperature increments have been plotted for one cell representing how much hotter the metal would have needed to be in order to dissolve the analyzed amounts of titanium and boron. It is clear that the metal temperature would have had to have been about 40°C above the measured value to provide for these Ti and B values at equilibrium. This is quite unreasonable, even taking into account periodic temperature increases accompanying anode effects and shorts.

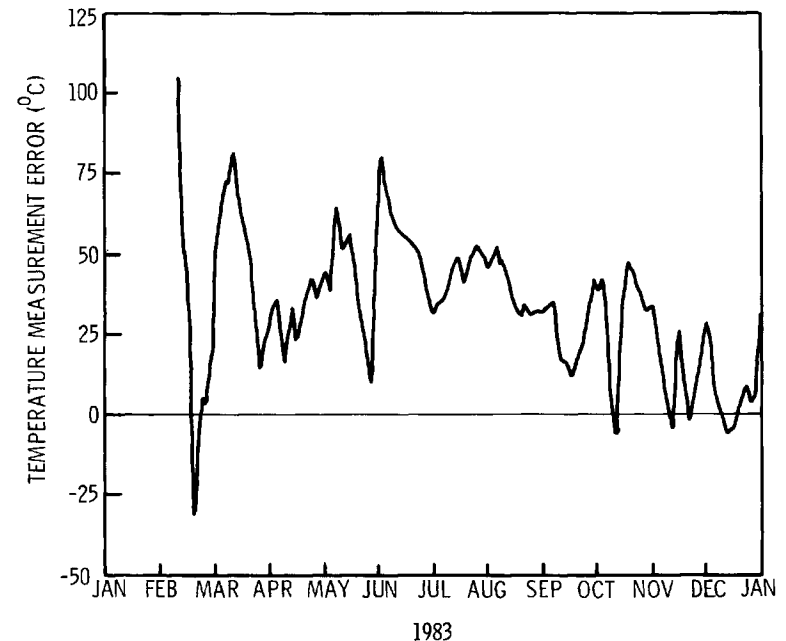


Figure 11

Calculated temperature measurement error required to account for the observed Ti and B analyses at equilibrium solubility

The proposition that other elements are present in the metal pad and precipitate with Ti and B is quite attractive because it permits an explanation for the data that is not tied directly to the solubility product. Thus, for example, Ti and B assays substantially over the solubility limit may arise because of the precipitation of TiX and/or BY (where X and Y are elements that form compounds with Ti and B that are insoluble in molten aluminum). If this precipitation takes place, the activities of Ti and B in the metal are effectively lowered, and TiB₂ will continue to dissolve until the solubility limit is reached. It is important to realize that this limit may indeed never be reached in practice, since the molten metal in an operating cell is continually being diluted by cathodically-produced aluminum.

In Figure 12 the total titanium analysis, the TiB_2 oversaturation, and the titanium excess over base level have been plotted against temperature for types A and B TiB_2 , respectively. These figures show that the temperature dependence of coating loss is quite different for the two materials. Detailed analysis has shown that coating wear is actually controlled by specific chemical and physical properties of the original TiB_2 powder.

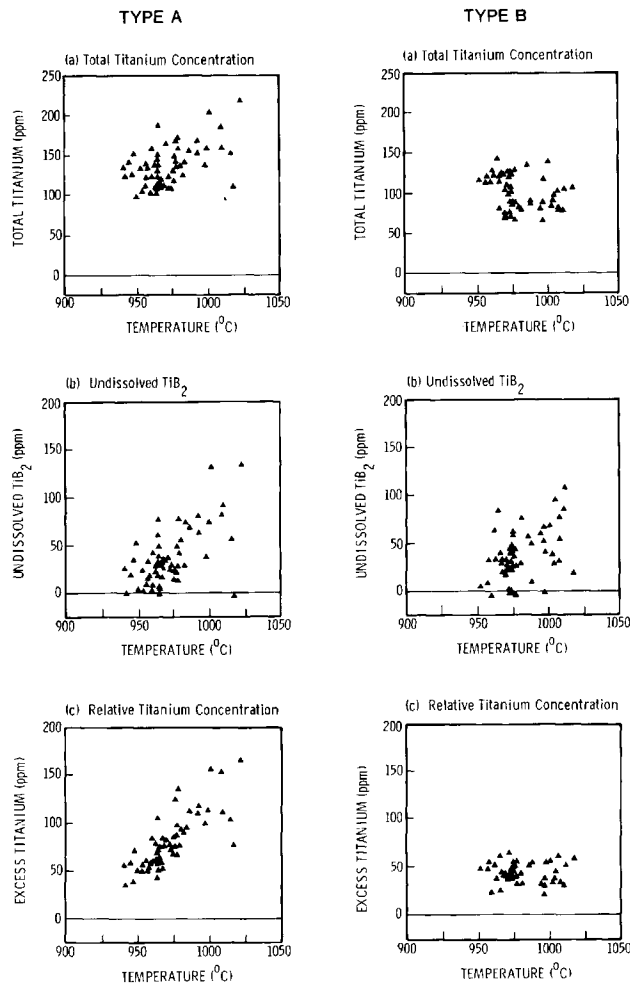


Figure 12
 TiB_2 loss parameters versus temperature for two different TiB_2 specifications.

Conclusions

The results of the 12-cell plant trial of the Martin Marietta carbon/ TiB_2 coating have reinforced many of the preliminary conclusions drawn in the earlier 6-cell test. The coated cathode test cells showed consistent benefits over the control group in cell voltage, current efficiency, and, hence, specific energy consumption. During major plant upsets, these benefits were overwhelmed by extraneous factors beyond the control of the operators. During normal operation, however, the test cells consumed approximately 0.15 kWh/lb less energy, and produced almost 2% more metal.

The operating personnel at the plant reported a definite preference for the TiB_2 -coated cells, because the cathode surface was always cleaner and when muck accumulated, it dispersed more rapidly because it did not adhere to the cell bottom. There was further objective evidence to this effect in that the cathode current distribution was consistently more uniform in the test group than in the control group.

Based on analyses for titanium and boron in the metal pad, the rate of TiB_2 loss from the cathode coating was extremely slow and uniform. A 5- to 7-year coating life is predicted depending on the TiB_2 type and the original coating thickness.

The coating wear mechanism is believed to be controlled by specific physical and chemical properties of the TiB_2 powder. The amount dissolved is only slightly above the solubility limit at any temperature, but the temperature dependence varies with the TiB_2 specifications.

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