The Effect of Preparation and Cleaning Techniques on Electrochemical Testing of Aluminium Anodes

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SUMMARY: When comparing the preparation and cleaning techniques of the various International Standards for electrochemical testing, there are considerable differences in the methods employed. Some standards lack sufficient detail, making them wide open to interpretation. This can result in significant variations in the test results achieved for both anode consumption rate and anode potential.

With the intention of determining a more comprehensive and standardised approach to anode sample preparation and cleaning, a series of A6 (AS2239) aluminium rod samples were cast and tested. Using the test method DNV-RP-B401 “Cathodic Protection Design” Annex B “Laboratory Testing of Galvanic Anode Materials for Quality Control” as the basis for the testing, we compared how various preparation and cleaning scenarios affected the anode consumption rate and anode potential.

This paper reviews the test method and key variables, then analyses and compares what effect preparation and cleaning has on anode consumption rate and anode potential.

Keywords: Aluminium, Anode, Electrochemical, Consumption, Potential

1. INTRODUCTION

The purpose of this paper is to question what effect preparation and cleaning techniques have on the electrochemical capacity and the closed circuit potential of Aluminium anode test samples.

This testing is the first step in examining the concentration and interrelationship between key elements within Aluminium anode alloys with the long term objective of identifying more effective combinations of elements to create a more efficient Aluminium anode alloy. Before this process could be undertaken, it was necessary to create a comprehensive, clearly defined procedure. Current Australian and International standards provide most of the details, but some information was missing, this testing was conducted to aid in creating a rigid, concise internal test procedure to ensure that all of our electrochemical testing results could be compared and reviewed with confidence that the process is clearly defined and standardised.

The paper will proceed as follows:
1. Compare and the main aspects of preparation and cleaning techniques identified in DNV-RP-B401, NACE TM0191 and AS2239
2. Review the test method
3. Review, discuss and compare the test results
4. Conclusion

2. COMPARISON OF SHORT TERM TEST METHODS

DNV-RP-B401, NACE TM0190 and AS2239 are internationally recognised standards which include short term electrochemical testing of aluminium anodes. Laboratory based electrochemical testing is a very sensitive testing process, where seemingly insignificant variations can affect the electrochemical capacity of the anode sample.

As table 1 illustrates, there are some similarities in the testing process of each standard, but there are also some significant differences, including the surface treatment, where the choice of machined or as-cast samples can affect the end result. Also of significance is the pre-test cleaning method. These two variables will be the focus of this paper, but it is worth keeping in mind that there are a number of other variables which can also have a significant effect. Some of these variables will be discussed towards the end of this paper.
Table 1. Comparison of Short Term Testing Methods

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Title</td>
<td>Cathodic Protection Design</td>
<td>Impressed Current Laboratory Testing of Aluminium Alloy Anodes</td>
<td>Galvanic (sacrificial) anodes for cathodic protection</td>
</tr>
<tr>
<td>Method</td>
<td>Mass Loss</td>
<td>Mass Loss &amp; Hydrogen Evolution</td>
<td>Mass Loss</td>
</tr>
<tr>
<td>Sample dimensions (exposed to test)</td>
<td>15.7cm²</td>
<td>16,000mm³ cubic sample cut from anode to be tested.</td>
<td>The surface area to be used to obtain current density is calculated from the initial dimensions of the sample</td>
</tr>
<tr>
<td>Individual samples cut to 3,900mm² surface area cast into sample moulds.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface Treatment</td>
<td>Machined</td>
<td>Saw cut surface for samples cut from anodes</td>
<td>As cast is preferred but cut and machined are acceptable.</td>
</tr>
<tr>
<td>Pre Test Cleaning</td>
<td>Rinsed in tap water followed by ethanol</td>
<td>Sodium Hydroxide then water</td>
<td>Nitric Acid then fresh water</td>
</tr>
<tr>
<td>Post Test cleaning</td>
<td>Chromium trioxide, phosphoric acid, water</td>
<td>Chromium trioxide (or Nitric Acid), phosphoric acid, water</td>
<td>Nitric Acid then fresh water</td>
</tr>
<tr>
<td>Test solution</td>
<td>Natural Seawater (adequate purity and salinity of min 30‰) or synthetic seawater ASTM D1141</td>
<td>Synthetic Seawater ASTM 1141</td>
<td>Clean Sea Water (resistivity no greater than 0.3Ohms at 20degC or Synthetic Seawater ASTM 1141</td>
</tr>
<tr>
<td>Volume of electrolyte</td>
<td>Min 10L</td>
<td>1.5L</td>
<td>Not specified</td>
</tr>
<tr>
<td>Cathode</td>
<td>Steel/stainless steel Minimum 20x the exposed area of the sample (minimum 400cm²)</td>
<td>Stainless Steel beaker or Carbon steel container</td>
<td>Aluminium or Stainless Steel</td>
</tr>
<tr>
<td>Temperature</td>
<td>20degC +/-3degC</td>
<td>23degC +/-3degC</td>
<td>Not specified</td>
</tr>
<tr>
<td>Test Duration</td>
<td>4 days</td>
<td>14 days</td>
<td>10 days or more</td>
</tr>
<tr>
<td>Electrochemical Capacity</td>
<td>Min 2,500 Ah/kg</td>
<td>2,623 to 2,949 Ah/kg (for Al-Zn-Hg alloy)</td>
<td>2,500 Ah/kg</td>
</tr>
<tr>
<td>Closed Circuit Potential (wrt Ag/AgCl Ref Electrode)</td>
<td>Less than or equal to -1050mV</td>
<td>-785 to -1069mV</td>
<td>At least -1050mV</td>
</tr>
</tbody>
</table>

Which method is right? There is no way to definitively answer this question. Even if a series of identical samples were cast from a single melt (which is almost impossible) and the samples were submitted to each of the test methods listed above, the results for each would most likely be different. There is no “best” or “correct” result.

3. TEST METHOD

3.1 DNV-RP-B401 Test Procedure

The testing procedure was based on the requirements of DNV-RP-B401. Where gaps or ambiguities were identified in the standard, Det Norske Veritas were happy to assist and provide direction. The testing process was discussed at length with Robin May (CMET Pty Ltd), who provided much assistance. Without his input this paper would not have been possible.

If you are interested in reviewing the test method, please refer to Annex B – Laboratory Testing of Galvanic Anode Materials for Quality Control of DNV-RP-B401 (2010) Cathodic Protection Design. The internal procedure fills some of the gaps and is sufficiently detailed to ensure that as many details as possible are controlled.

Note that the DNV-RP-B401 standard was not followed with the post treatment cleaning. In each test the corrosion by-product was removed with a nylon brush and running water. The DNV-RP-B401 standard specifies cleaning with Chromium trioxide, phosphoric acid then water. The decision was made to avoid this method on OH&S grounds, as Chromium Trioxide is a known carcinogen and explodes in the presence of organic compounds and solvents.

Secondly, the use of Chromium trioxide and phosphoric acid has been questioned, as it may remove excessive amounts of aluminium alloy, which of course would skew the consumption rate test results.
Post cleaning is a variable which was not included in the study. It is an aspect of the cleaning process which does require further attention. This will be investigated in the near future.

### 3.2 Anode Test Samples

For the purposes of this paper, a series of anode rod samples were cast in the AS2239 A6 alloy, which is derived from the commonly used Galvalum®III alloy. A6 complies with the Galvalum®III specification, but has more stringent restrictions on impurities. Refer to table 2 below for the A6 alloy composition.

#### Table 2. AS2239 A6 Alloy Composition

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Zn</th>
<th>In</th>
<th>Cd</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mg</th>
<th>Ti</th>
<th>Sn</th>
<th>Other Each</th>
<th>Tot.</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS2239</td>
<td>2.0 – 6.0</td>
<td>0.01 – 0.02</td>
<td>0.005 max</td>
<td>0.08 – 0.12</td>
<td>0.12 max</td>
<td>0.006 max</td>
<td>0.02 max</td>
<td>0.02 max</td>
<td>0.02 max</td>
<td>0.02 max</td>
<td>0.05</td>
<td>Bal</td>
</tr>
</tbody>
</table>

Five sets of tests were conducted using the A6 alloy and also a single test on a sample cut from a PO610 Aluminium Ingot, which is the primary aluminium ingot used as the basis to manufacture the A6 alloy. This test was included to provide some context for the results. It clearly illustrates the difference between an alloy designed to offer cathodic protection and the pure ingot which does not offer cathodic protection due to the passive film forming on the surface which acts as a barrier.

Test 5 samples were cut from within an anode. It was included so that a comparison could be made between test results from an actual anode and rod samples which are cast into small diameter rod moulds.

In order to minimise the effects of individual test sample results, 4 samples of each were tested for each of the first 5 scenarios (refer to table 3 below). Test 6 data was based on results from a single sample.

### 4. TEST RESULTS

#### Table 3. Summary of Test Results

<table>
<thead>
<tr>
<th>Surface Preparation</th>
<th>Test 1</th>
<th>Test 2</th>
<th>Test 3</th>
<th>Test 4</th>
<th>Test 5</th>
<th>Test 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre Test Treatment</td>
<td>As-Cast</td>
<td>As-Cast</td>
<td>Machined</td>
<td>Machined</td>
<td>Saw Cut</td>
<td>Machined</td>
</tr>
<tr>
<td>Post Test Treatment</td>
<td>Ethanol then Tap water</td>
<td>Sodium Hydroxide then Nitric Acid</td>
<td>Ethanol then Tap water</td>
<td>Sodium Hydroxide then Nitric Acid</td>
<td>Sample cut from within A6 anode</td>
<td>Sample cut from PO610 ingot</td>
</tr>
<tr>
<td>Echem Capacity (Average for 4 tests)</td>
<td>2,718 Ah/kg</td>
<td>2,711 Ah/kg</td>
<td>2,692 Ah/kg</td>
<td>2,780 Ah/kg</td>
<td>2,742 Ah/kg</td>
<td>2295 Ah/kg</td>
</tr>
<tr>
<td>Potential Readings</td>
<td>-1059mV</td>
<td>-1062mV</td>
<td>-1046mV</td>
<td>-1054mV</td>
<td>-1083mV</td>
<td>-688mV</td>
</tr>
<tr>
<td>Polarisation Time</td>
<td>Almost immediately</td>
<td>Almost immediately</td>
<td>5+ hours</td>
<td>3 ½ hours</td>
<td>72+ hours</td>
<td>Almost immediately</td>
</tr>
</tbody>
</table>

Table 3 indicates that for the 5 anode alloys (Tests 1 to 5) the electrochemical test results vary by 88Ah/kg and the potential readings at the conclusion of the 96hr test period are quite stable, varying by only 37mV. “As-cast” samples polarised immediately, while machined samples took a lot longer to polarise. These results are reviewed in more detail below.
4.1 Consumption Rate

Chart 1. Consumption Rate Comparison (Ah/kg)

<table>
<thead>
<tr>
<th>Test Description</th>
<th>Consumption Rate (Ah/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEST 1 As Cast (Ethanol &amp; Water)</td>
<td>2718</td>
</tr>
<tr>
<td>TEST 2 As Cast (NaOH HNO3)</td>
<td>2711</td>
</tr>
<tr>
<td>TEST 3 Machined (Ethanol &amp; Water)</td>
<td>2692</td>
</tr>
<tr>
<td>TEST 4: Machined (NaOH HNO3)</td>
<td>2780</td>
</tr>
<tr>
<td>TEST 5 Machined Anode (Ethanol &amp; Water)</td>
<td>2742</td>
</tr>
<tr>
<td>TEST 6 Ingot (Ethanol &amp; Water)</td>
<td>2295</td>
</tr>
</tbody>
</table>

To provide some context to the results, the DNV-RP-B401 standard specifies a minimum electrochemical capacity of 2,500 Ah/kg. The results in Chart 1 should be viewed with this baseline in mind. It is evident that all anode alloys (Test 1 to 5) easily pass the DNV-RP-B401 benchmark. As expected the PO610 primary ingot (Test 6) did not. The effect the various preparation and cleaning scenarios have in relation to each other will be discussed.

Observation 1: The chemical etch counteracts the effect of the machining. The machined sample which was treated with Sodium Hydroxide and Nitric Acid (Test 4) was 88 units higher than the equivalent sample which was pre cleaned in ethanol and water (Test 3).

Observation 2: A comparison between Test 3 and Test 5 indicates a difference of 50 units. Both samples were machined and both were washed in ethanol and water. The significant difference is that the Test 3 samples were cast into a narrow diameter rod mould, while Test 5 samples were cast into a large cross sectioned mould and the samples were cut from deep within the anode. The significant difference in results could be due to one of two factors:

1. The difference between the microstructure of the two samples, as a result of the different mould sizes and therefore casting modulus. This would bring into question the significance of casting rod samples to represent actual large cross-section anode.
2. The aggressive “cutting” of the anode surface employed to remove the Test 5 samples from deep within the anode caused severe damage to the outer surface of the sample which caused reduced weight loss and therefore a higher consumption rate.

Further testing is required to identify which is the more significant factor. Follow up papers will focus on this topic.

Observation 3: Test 1 and test 2 were both “as-cast” with the key variable being that test 1 was cleaned in ethanol and water, while test 2 was chemically etched. The difference between the two consumption rates was 26 Ah/kg. It appears that the chemical etch has minimal effect on as-cast samples. This is supported later in this paper where we examine photographs of the wear patterns at the conclusion of the 96hr test period.
4.2 Electrochemical Potential

Chart 2. Electrochemical Potential Comparison (mV)

- TEST 1 As Cast (Ethanol & Water)  -1059
- TEST 2 As Cast (NaOH HNO3)  -1062
- TEST 3 Machined (Ethanol & Water)  -1046
- TEST 4 Machined (NaOH HNO3)  -1054
- TEST 5 Machined Anode (Ethanol & Water)  -1083
- TEST 6 Ingot (Ethanol & Water)  -688

Chart 2 illustrates that regardless of whether the samples have been machined, “as-cast” or whether the pre test cleaning process has been chemically etched or just washed in ethanol and water, by the end of the 96hr test period, each of the anode alloys (Tests 1 to 5) was close to or more negative than the -1050mV mark desired for anode potential. Chart 2 also clearly illustrates that in terms of achieving a desirable anode potential, pure aluminium ingot falls a long way short (-688mV).

When comparing the rate at which each of the anode samples polarised (refer to Table 3), machining clearly inhibits polarization. Note that for the 3 machined scenarios (Tests 3, 4 and 5), the samples took hours to polarise, compared to the “as-cast” samples (Tests 1 and 2), which polarized almost immediately.

This is a problem for anodes in service. Areas of anodes that have been machined, worked with a grinder or hammered often passivate, while the remaining areas of the anode happily corrode. For this reason, many tender specifications clearly state that anodes must not be machined, worked with a grinder or hammered.

Machining the anode surface has an effect in two ways. Firstly the “folding over” of the material can compress oxide layer over oxide layer. Secondly, there is a possibility that heat generated during machining can cause precipitation of a solid solution. The final turns in the lathe on a 10mm dia test bar become quite hot (80-120 deg C). This can encourage higher driving potential but may also encourage a faster consumption rate. This is being investigated further.

4.3 Wear Pattern

Chart 3. Wear Pattern at Conclusion of 96hr Test

Test 1: As cast (Ethanol & Water Clean)
Test 2: As cast (NaOH HNO3 Clean)

Test 3: Machined (Ethanol & Water Clean)

Test 4: Machined (NaOH HNO3 Clean)
Observation 1: Chart 3 indicates that the as-cast samples (Test 1 and 2) both show a similarly even corrosion pattern. There is little difference between Test 1, which was pre-cleaned with ethanol and water and Test 2 which was chemically etched.

Notably, these samples are “as-cast”, but the Test 1 photograph indicates that 3 of the 4 test samples have areas of passivation. The samples were finished to remove excess aluminium just after casting. This photograph supports the previous discussion in section 4.2 that machining damages the anode surfaces and reduces the efficiency of the anode.

Observation 2: Tests 3, 4 and 5 were all machined. The corrosion pattern is far more uneven compared to the as-cast samples (Test 1 and 2), with large sections of passivation. As discussed previously, this is a visual representation of how machining has a detrimental effect on the efficiency of the anode.

The A6 alloy (plus Galvalum®III and A1) does not machine as engineering grades of Aluminium would. Engineering grades are manufactured with alloy content and “modifying elements” to promote a particular microstructure, one that produces even “cutting”. When machining these anode alloys, it tends to build up on the tool. It then “pastes” itself to the gap between the tool and the sample, which results in the swarf doing the cutting (quite brutally) rather than the tool. This causes “folding over” of the oxide layers and results in the almost impenetrable finish.

During “sacrificial corrosion” these areas are then “undermined” by corroding material until the entire piece falls away (refer to the example in Figure 1, below), hence a higher weight loss and a lower consumption rate. This is particularly evident in Tests 3 and 5 (Chart 3), where deep craters are visible adjacent to passive areas.

Also, there is the problem with precipitation (solid solution) from the machining process (as discussed in section 4.2 above) it may help to explain why some samples show “grand canyon” corrosion right alongside original machining marks. The machining marks are where material has been forced over, almost welded together, the corrosion “canyons” where the material has broken away.

Tests 3 and 5 samples were washed in ethanol and water, while Test 4 underwent a chemical etch. It is evident that the chemical etch had the effect of breaking down some of the “damage” caused by the machining.

Observation 3: The Test 5 photograph (Chart 3), shows the samples which were cut from within an actual anode. The surface of each sample was clearly “damaged” by the saw cut and large sections have passivated. It appears that well over 50% of the surface has passivated, which is a similar percentage to Test 3, which was also machined and cleaned in Ethanol then tap water.
5. CONCLUSION

5.1 Key Findings

- The chemical etch had little effect on “as-cast” samples.
- Regardless of whether the samples were machined, chemically etched, “as-cast” or cut from within an anode, if the chemical composition is right the anode potential was achieved by the end of the 96hr test cycle.
- “As-cast” anode samples all polarised almost immediately, while all machined anode samples took hours to polarise.
- Machined anode samples had large passive areas, which consequentially reduced the efficiency of the anode. The chemical etch appears to have “repaired” some of the damage caused by machining.

5.2 Discussion

Can the short term DNV-RP-B401 electrochemical test in a strictly controlled laboratory environment truly represent an anode attached to a subsea structure? A number of comments regarding the value of this testing have been made in recent times. Some suggest that it is an expensive and time consuming exercise which does not accurately represent an in service anode. The alternative view is that at the time of manufacture, a measure of confidence that the anodes will perform once installed is essential. Short term electrochemical testing is one piece of the puzzle that provides this confidence.

According to the DNV-RP-B401 benchmarks of 2,500Ah/kg for the consumption rate and -1050mV for the anode potential, it is clear that all of the anode samples tested as part of this paper were successful, whilst the ingot (not an anode alloy), was nowhere near these benchmarks. The DNV-RP-B401 short term test should be used as a basic test for quality control purposes only. It becomes largely irrelevant when the aim of the testing is to produce a more efficient anode. It simply does not have the resolution required to provide conclusive results.

As the test results started to accumulate, it became clear that the parameters of our test method were insufficient for what we were attempting to test. For our purposes the DNV-RP-B401 short term test method was far too short (4 days), and the size of the samples and the volume of electrolyte are too small to provide clear cut results. It is clear that in order to move forward with our testing we will need to revise some of the fundamental aspects of the test method.

This paper covered some of the variables related to sample preparation and cleaning. It is just the starting point from which further research is required. Since writing this paper testing has commenced on a wider range of variables including mould size (modulus), mould temperature and temperature of the alloy. All of these variables significantly influence the grain structure of an anode and therefore the electrochemical capacity.

These variables and the contents of this paper have not even touched on the concentration of particular elements and the interrelationship of elements such as Silicon, Iron and Indium within the alloy material. Clearly there is much research to be done.

6. ACKNOWLEDGEMENTS

Thank you to Robin May (CMET Pty Ltd). Without his input this paper would not have been written.

7. REFERENCES

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<thead>
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<tr>
<td>Standard</td>
<td>AS2239 (2003) Galvanic (sacrificial) anodes for cathodic protection</td>
</tr>
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</table>
8. AUTHOR DETAILS

Brent Linde (B App. Sci) is the Marketing and Product Development Manager at Cathodic Diecasting, where he has been employed since May 2008. He has been part of the Anode Manufacturing industry for over 14 years. Over that time he has developed an intimate understanding of manufacturing and laboratory processes.

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